

VOLUME 34

JANUARY 1956

NUMBER 1

Canadian Journal of Chemistry

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CANADIAN JOURNAL OF CHEMISTRY

(Formerly Section B, Canadian Journal of Research)

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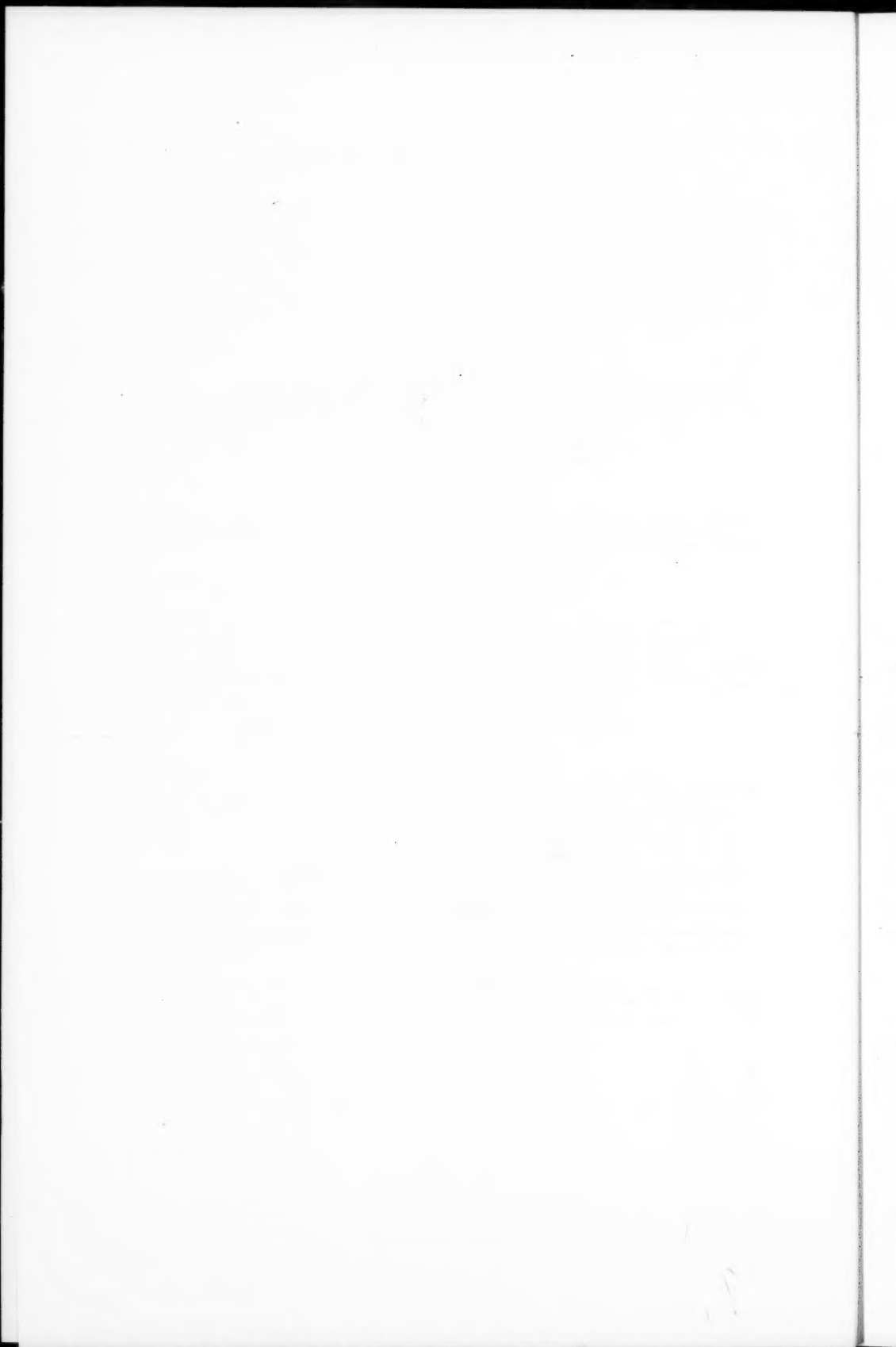
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OTTAWA CANADA**



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VOLUME 34

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NUMBER 1

THE ALKALOIDS OF FUMARIACEOUS PLANTS

LI. CORYDALIS SOLIDA (L.) SWARTZ¹

By R. H. F. MANSKE

ABSTRACT

Only six alkaloids, namely protopine, allocryptopine, corydaline, *d*-stylopine, *dl*-tetrahydropalmatine, and aurotensine, could be isolated from this plant. The total yield of alkaloids was approximately 0.06%. Chemically, the plant is closely allied with *Corydalis ambigua* and both had been relegated to the same botanical section of the genus.

The section *Pes-gallinaceus* Irmish of the genus *Corydalis* Vent. includes those representatives in which the root is bulbous and does not become hollow. The best known representative is *C. solida* (L.) Swartz which is widespread throughout temperate Europe. Many minor variations have given rise to an extensive synonymy the most common of which is *C. bulbosa* DC.

It has been examined by Haars (1) who claimed the presence of bulbocapnine and by Heyl (2) who found protopine and two bases melting at 145° and 132° respectively, but has not been further characterized. In the writer's experience this plant is the least rewarding of any in the entire genus. Not only is the total alkaloid content very low (about 0.06%) but only six alkaloids could be definitely identified and these are all known ones, namely protopine, allocryptopine, corydaline, *dl*-tetrahydropalmatine, *d*-stylopine, and aurotensine. These constituents are much the same as those of *C. ambigua* Cham. and Schlecht. (4) and it is perhaps significant that the two plants under discussion belong to the same section.

EXPERIMENTAL

The material for the present investigation was grown in a local garden and the crops collected annually for several successive years. In all cases the aerial portion (7.9 kgm.) was collected at the time the seeds were just approaching maturity. The tubers (6.7 kgm.) were collected at various times of the year. The two portions were worked up separately but no quantitative or qualitative differences were evident.

The procedure for isolating the various alkaloids was the same as that repeatedly used by the writer (3).

¹Manuscript received October 3, 1955.

Contribution from the Dominion Rubber Company Limited Research Laboratories, Guelph, Ontario.

Protopine and Allocryptopine

The fraction (BS) of nonphenolic alkaloids whose hydrochlorides are insoluble in chloroform was purified by dissolution in dilute acid and regenerating the free bases with ammonia in the presence of a large volume of ether. The residue from the ether extract crystallized readily in contact with methanol and when recrystallized once from chloroform-methanol the resultant protopine melted at 210°C.* either alone or in admixture with an authentic specimen. The small amount of protopine remaining in the methanolic filtrate was separated as its sparingly soluble nitrate and the base then remaining in solution regenerated again by the addition of ammonia in the presence of ether. The residue from the washed ether solution in contact with methanol crystallized at once when inoculated with a crystal of allocryptopine and when recrystallized once from methanol the base melted at 160° either alone or in admixture with authentic allocryptopine. The yield of protopine was *ca.* 0.014% and that of allocryptopine was *ca.* 0.005%. Neither cryptopine nor any further bases could be isolated from the fraction under discussion.

Corydaline

The fraction BC consists of nonphenolic alkaloids whose hydrochlorides are extractable from aqueous solution by means of chloroform. When it was purified by taking through dilute acid and regenerating with ammonia and extracting with ether there was obtained a pale yellow resin which readily crystallized in contact with methanol. The characteristic elongated hexagonal plates thus obtained were recrystallized once from hot methanol and then melted sharply at 135°C. Admixture with *d*-corydaline did not lower the melting point. The yield was *ca.* 0.02%. This is probably Heyl's alkaloid of *m.p.* 132°.

d-Stylopine

The filtrate from the crystallization of the corydaline deposited a very sparingly soluble base in the course of several days. When it was recrystallized from chloroform-methanol it consisted of colorless prisms which melted sharply at 202°C. either alone or in admixture with *d*-stylopine. The yield was less than 0.002%.

dl-Tetrahydropalmatine

When the mother liquors from the *d*-stylopine were freed of organic solvent and the residue dissolved in hot dilute hydrochloric acid there was formed a sparingly soluble hydrochloride. This was recrystallized from hot water and the base from it recrystallized from methanol. The almost colorless crystals then obtained melted at 150°C. and when they were admixed with *dl*-tetrahydropalmatine there was no alteration in melting point. The yield was about 0.01%. This may be Heyl's alkaloid of *m.p.* 145°.

Aurotensine

The phenolic fractions (BSE and EES) of the alkaloids whose hydrochlorides are not dissolved by chloroform were combined and converted to

*All melting points are corrected.

hydrochloride in methanol. The base regenerated from the hydrochloride crystallized in contact with methanol and when recrystallized from the same solvent was obtained in almost colorless rectangular plates which, either alone or in admixture with aurotensine, melted at 128°C. The yield was less than 0.001%.

By reworking other fractions and the mother liquors it was possible to obtain roughly the above yields. It is more than likely that other bases are elaborated by the plant under scrutiny but since the total uncrystallized portion weighed less than one gram there can only be traces of other alkaloids. Bulbocapnine definitely seems to be absent.

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THE POLAROGRAPHY OF THE MONOXIMES AND DIOXIMES OF BENZOQUINONE, NAPHTHOQUINONE, AND ANTHRAQUINONE¹

BY R. M. ELOFSON² AND J. G. ATKINSON³

ABSTRACT

The polarographic behavior of the monoximes and dioximes of 1,4-benzoquinone, 1,4-naphthoquinone, 1,2-naphthoquinone, and 9,10-anthraquinone has been investigated in the pH range 3 to 14. All of the compounds produce well-defined polarographic reduction waves which can be used for analytical purposes. Polarographic evidence indicates that the monoximes and the dioximes exhibit tautomerism.

INTRODUCTION

In this investigation the polarography of the monoximes and dioximes of 1,4-benzoquinone, 1,4-naphthoquinone, 1,2-naphthoquinone, and 9,10-anthraquinone over the pH range 3 to 14 has been studied. Because of the structural relationship of the monoximes with nitroso compounds, the polarography of nitrosobenzene has been reinvestigated.

The polarography of 9,10-anthraquinone monoxime (17), 1,4-benzoquinone monoxime (2), and 1,2-naphthoquinone-1-monoxime (8) has been determined previously and separately over different pH ranges. Recently, Souchay and Ser (15), and Calzolari (5) have reported systematic polarographic investigations of the oximes of aromatic ketones. The oxidation-reduction potential of nitrosobenzene has been previously determined by electromotive force measurements by Lutz and Lytton (10) and by polarographic methods by Holleck and Exner (6). No work has been reported on the polarography of the quinone dioximes.

EXPERIMENTAL

Apparatus

A Leeds and Northrup Electrochemograph Type E was used to record the polarograms. A minimum of damping was employed (position 1) to prevent distortion of the waves.

The capillaries that were used were made from marine barometer tubing obtained from the Corning Glass Works. For the data portrayed in Tables I, II, and IV, the value of h was 54.6 cm., t was 4.13 sec., and m was 2.36 mgm./sec. at zero applied voltage vs. saturated calomel electrode in pH 7 buffer and 50% ethanol at 25° C.

The electrolysis cells were of the usual type. A saturated calomel electrode was used as the anode, connected by means of a flexible saturated potassium chloride agar bridge to the electrolysis cell.

¹Manuscript received August 22, 1955.

Contribution from the Research Council of Alberta, Edmonton, Alberta.

²Senior Research Chemist, Research Council of Alberta, Edmonton, Alberta.

³Laboratory Assistant, Research Council of Alberta, Edmonton, Alberta.

Media

Buffers were prepared according to Clark and Lubs; pH measurements of alcohol mixtures were recorded with a Beckman Model G pH meter and glass electrode.

Chemicals

1,4-Benzoquinone monoxime, m.p. 136–138° C. (decomp.), and 1,4-benzoquinone dioxime, m.p. 247–248° C. (decomp.), were prepared according to Beilstein.

9,10-Anthraquinone monoxime, m.p. 222–223° C. (decomp.), was prepared according to Julian (7).

9,10-Anthraquinone dioxime was prepared by treating 5 gm. 9,10-anthraquinone with 10 gm. hydroxylamine hydrochloride in 50 ml. of pyridine; the yield was quantitative. Upon recrystallization from methanol it melted at 259–260° C. (decomp.) (11).

1,2-Naphthoquinone-2-monoxime, m.p. 165–167° C. (decomp.), and 1,4-naphthoquinone monoxime, m.p. 190–192° C. (decomp.), were prepared according to Beilstein from α -naphthol.

1,2-Naphthoquinone dioxime, m.p. 150° C. (decomp.), and 1,4-naphthoquinone dioxime, m.p. 221° C. (decomp.), were prepared from the corresponding monoximes by treatment with hydroxylamine hydrochloride and pyridine in alcohol according to Beilstein.

Nitrosobenzene, m.p. 66.5–68° C., was purified by recrystallization from ether.

RESULTS

The Polarography of Nitrosobenzene

In Table I are tabulated the half-wave potentials of nitrosobenzene over the pH range 6 to 11.

TABLE I
HALF-WAVE POTENTIALS OF NITROSOBENZENE VS. S.C.E.
Concentration 0.9×10^{-4} M approx.

A. Water solution					
pH	6	7	9	10	
$-E_1$ volts	0.012	0.075	0.185	0.245	
B. Alcohol 58% by volume					
pH	6.3	8.3	10.4	11.4	0.1 N NaOH
$-E_1$ volts	0.072	0.190	0.320	0.380	0.480

The first series of measurements carried out in aqueous solution obey equation [1]:

$$E_1 \text{ vs. S.C.E.} = +0.339 - 0.0584 \text{ pH.} \quad [1]$$

This represents the reversible nitrosobenzene-phenylhydroxylamine system whence the normal electrode potential E_0 becomes $0.339 + 0.246 = 0.585$ v.,

which is in excellent agreement with the results of Lutz and Lytton (10) who obtained E_s equal to 0.582 v. by potentiometric titration.

In alcohol solution the relationship between the half-wave potential and the pH as measured with the glass electrode is exactly linear but the equation is given by [II]:

$$E_s \text{ vs. S.C.E.} = +0.323 - 0.0603 \text{ pH}, \quad [\text{II}]$$

whence E_s becomes 0.569 volts. The discrepancy in the results, which amounts to about 50 mv. in the actual measurements, is presumably partly due to the errors of measuring pH with the glass electrode in nonaqueous solutions. Similar considerations would probably apply to the other measurements recorded in this paper.

Because of the high volatility of nitrosobenzene exact diffusion current measurements were not made, but the wave heights indicated quite clearly that two electrons were involved in the reduction. This was also evident from a plot of E_s vs. $\log [i/(i_d - i)]$. Straight lines were obtained with a slope of 27 mv. at pH 7 and 31 mv. at pH 10, which agree well with the theoretical value of 29 mv. for a two-electron reduction.

The Polarography of the Quinone Dioximes

The half-wave potentials of the quinone dioximes in alcohol solution are presented in Table II. All the dioximes were reduced in acid solutions and in strongly alkaline solutions by a process involving six electrons. This was established by comparing the wave heights for anthraquinone dioxime and benzophenone in tetramethylammonium hydroxide solution. Under these

TABLE II
HALF-WAVE POTENTIALS VS. S.C.E. OF QUINONE DIOXIMES
Concentration $1.67 \times 10^{-4} M$ in 55% ethanol
(minor waves in brackets)

pH	Dioximes							
	1,4-Benzo- quinone		1,4-Naphtho- quinone		1,2-Naphtho- quinone		9,10-Anthra- quinone	
	$-E_s$, volts	n^*	$-E_s$, volts	n^*	$-E_s$, volts	n^*	$-E_s$, volts	n^*
3.1	0.09	6	0.13	6	0.07	6	0.37	6
3.9	0.16	6	0.21	6	—	—	0.49	6
5.3	0.30	—	0.34(0.47)	6	0.30	6	0.61	6
6.3	0.39(0.52)	—	—	—	—	—	—	—
7.3	0.54	—	0.51	6	0.38	6	0.72	6
8.4	0.80	—	—	—	0.48	—	0.82	6
9.4	(0.79)0.96	—	(—)0.95	—	0.61(—)	—	0.86(—)	—
10.4	1.10	6	1.01	—	(0.82)1.02	—	(—)1.27	—
11.4	—	—	—	—	1.05	6	1.32	6
0.1 N NaOH	1.12	6	1.26	6	1.15	6	1.38	6
0.05 M (CH ₃) ₄ NOH	1.11	6	1.14	6	1.09	6	1.38	6

*Number of electrons.

conditions a $2.7 \times 10^{-4} M$ solution of benzophenone produced a wave of 1.31 μ a. and a $0.9 \times 10^{-4} M$ solution of anthraquinone dioxime produced a

wave of $1.30 \mu\text{a}$. Since the number of electrons required for the polarographic reduction of benzophenone in alkaline solution is known to be two, it follows that the number of electrons required in the reduction of anthraquinone dioxime must be six. The corresponding value for a $0.9 \times 10^{-4} M$ solution of benzoquinone dioxime was $1.36 \mu\text{a}$ under the same conditions. At a pH of 3.1 the diffusion currents of $0.9 \times 10^{-4} M$ solutions of 1,4-benzoquinone dioxime and 9,10-anthraquinone dioxime in the same concentration of alcohol were respectively 1.32 and $1.26 \mu\text{a}$. Therefore it follows that the number of electrons required at the low pH is likewise six. The height of the reduction wave of both of the naphthoquinone dioximes likewise corresponded to the assignment of six-electron reduction waves at low and high pH's.

The surprising equality of the diffusion currents for anthraquinone dioxime and benzoquinone dioxime, despite the fact that the molecular weight of the former was much larger than that of the latter, prompted a controlled potential analysis of anthraquinone dioxime. This was carried out with a $0.001 M$ solution in 50% ethyl alcohol and buffer of pH 4. A stirred mercury pool was used as cathode and a saturated calomel electrode as anode in order to prevent formation of oxygen. After electrolysis for 12 hr. no cathodic current remained on a test polarogram. Instead, an anodic wave was obtained at -0.20 v . The original cathodic current was $20 \mu\text{a}$. The anodic current was $6.5 \mu\text{a}$ or almost exactly one-third of the original cathodic wave. Anthrahydroquinone produced an anodic wave under these conditions at about -0.4 v . Since the diamine would have a higher oxidation potential than the anthrahydroquinone, that is, a more positive polarographic oxidation potential, the anodic wave corresponds to the wave of the expected diamine. Further confirmation of this hypothesis resulted when the alcohol was removed under vacuum and a reddish-brown powder was obtained which decomposed at 190°C .; reported m.p. for anthracenediamine 196°C . (14). The powder dissolved in hydrochloric acid and, upon heating, anthraquinone—identified by melting point $270\text{--}275^\circ \text{C}$. with sublimation—was precipitated out (18).

Variation of the height of mercury in the column showed that the height of the reduction waves varied with the square root of h (Table III). This indicates that the waves are diffusion-controlled in both acid and alkaline solutions.

At intermediate pH's the polarograms may show reduction in two steps and the total height of the waves does not correspond to an integral number of electrons. Detailed examination of these waves showed that the lower wave was rate-controlled, while the upper wave was diffusion-controlled, at least when it was the dominant wave. This was proved by the fact that the height of the lower wave was independent of the height of mercury in the reservoir while the height of the upper wave varied with the square root of the height of mercury in the reservoir as shown in Table III.

Kolthoff and Liberti (9) observed similar behavior in the polarographic reduction of N-nitrosophenylhydroxylamine. These authors attributed the kinetic current to the fact that the lower wave corresponded to the reduction of the neutral molecule and the higher wave to reduction of the anion. How-

TABLE III
EFFECT OF MERCURY HEIGHTS ON REDUCTION WAVES OF QUINONE DIOXIMES
Concentration $0.9 \times 10^{-4} M$ in 50% ethanol

Dioxime	pH		Current, μa .		Ratio* of current at h_2/h_1
			$h_2 = 55.6 \text{ cm.}$	$h_1 = 35.6 \text{ cm.}$	
9,10-Anthraquinone	3.1		1.54	1.26	1.22
1,4-Benzoquinone	3.1		1.68	1.32	1.27
1,4-Benzoquinone	10.4	Upper	1.32	1.06	1.25
		Lower	0.38	0.38	1.00
9,10-Anthraquinone	10.4	Upper	1.36	1.12	1.21
		Lower	0.25	0.25	1.00
1,4-Benzoquinone	7.3		0.62	0.62	1.00

* $\sqrt{(h_2/h_1)} = 1.25$.

ever, at the intermediate pH's the concentration of the neutral molecule was calculated to be much smaller than that which corresponded with the height of the reduction wave attributed to it. The height of this wave then corresponded with the rate of formation of the neutral molecule from the anion. Similar behavior has been observed with pyruvic acid and has been attributed by Brdicka (4) to slow formation of the undissociated acid from the anion at the electrode.

However, while the behavior of the quinone dioximes resembles that of these compounds, the kinetic waves cannot arise from the same reason since the dissociation constants are much smaller ($k = 10^{-10}$ to 10^{-12}) than for the compounds just discussed. This fact suggests that isomerization takes place at the electrode at intermediate pH's before reduction occurs. This will be discussed more fully in a subsequent section.

The diffusion currents vary directly with concentration in both acid and alkaline solutions over the concentration range studied of about 0.9 to $1.67 \times 10^{-4} M$. At intermediate pH's the waves may be indefinite enough to make quantitative measurement difficult.

The variation of the half-wave potentials with concentration has not been studied in detail. In acid solutions the half-wave potential of anthraquinone dioxime varies markedly with concentration. Changing the concentration from $0.9 \times 10^{-4} M$ to $1.67 \times 10^{-4} M$ changes the half-wave potential 0.22 v., whereas with benzoquinone dioxime the variation is much less than 0.01 v. for a similar change. In alkaline solutions the half-wave potentials are independent of concentration.

The Polarography of the Quinone Monoximes

The half-wave potentials of the quinone monoximes at various pH values in 55% ethanol are presented in Table IV. Inspection of the table shows that reduction involves four electrons at all pH values for the four compounds, with the exception of 1,4-benzoquinone monoxime at low pH values and 1,4-naphthoquinone monoxime at pH 10.4 and 11.4. In the latter cases the height of the waves is somewhat smaller than that corresponding to four-electron reductions. Previous workers have reported four-electron reduction for benzoquinone monoxime (2) and anthraquinone monoxime (17).

TABLE IV
HALF-WAVE POTENTIALS VS. S.C.E. OF QUINONE MONOXIME
Concentration $1.67 \times 10^{-4} M$ in 55% ethanol
(minor waves in brackets)

pH	Monoximes							
	1,4-Benzoquinone		1,4-Naphthoquinone		1,2-Naphthoquinone		9,10-Anthraquinone	
	$-E_1$, volts	n^*	$-E_1$, volts	n^*	$-E_1$, volts	n^*	$-E_1$, volts	n^*
3.1	—	—	—	—	0.02	4	0.23	4
3.9	0.04	—	0.13	4	0.05	4	0.29	4
5.3	0.14	—	0.25	4	0.16	4	0.38	4
7.3	0.24	(4)	0.31	4	0.23	4	0.48	4
8.4	0.31	4	0.35	4	—	—	0.59	4
9.4	0.46	0.63 4	0.41	4	0.35	4	0.58	4
10.4	()	0.90 4	0.56	0.75 —	—	—	0.63	4
11.4	0.88	4	()	0.81 —	0.55	4	0.68	4
0.1 N NaOH	0.82	4	0.88	4	0.65 & 0.78	4	0.91	4

*Number of electrons.

The fact that four electrons are involved in the reductions was established not only by comparison with the dioximes but by comparison with *p*-nitrophenol, the polarography of which has been elucidated by Astle and McConnell (2) and by Stocesova (16). In 0.1 N NaOH and 50% ethanol the current due to *p*-nitrophenol at a concentration of $0.9 \times 10^{-4} M$ was 1.48 μ a. and to benzoquinone monoxime at the same concentration was 1.0 μ a. Since the reduction of *p*-nitrophenol in alkaline solutions involves six electrons, the reduction of the quinone monoxime involves four electrons.

The reduction of the quinone monoximes proceeds in single steps in acid solutions. In alkaline solutions one wave only is obtained except in the case of the monoxime of 1,2-naphthoquinone in which a stepwise reduction occurs. 9,10-Anthraquinone monoxime provides only one reduction wave at all pH's studied. The other compounds show double waves in the pH range 9 to 11.

TABLE V
EFFECT OF MERCURY HEIGHT ON REDUCTION WAVES OF QUINONE MONOXIMES
Concentration $0.9 \times 10^{-4} M$ in 50% ethanol

Monoxime	pH		Current, μ a.		Ratio* of current at h_2/h_1
			$h_2 = 5.6$ cm.	$h_1 = 35.6$ cm.	
1,4-Benzoquinone	4.3	Lower Upper	1.4	1.3	1.07
1,4-Benzoquinone	9.4		0.48	0.48	1.00
			1.4	1.0	1.4
			1.68	1.34	1.25
9,10-Anthraquinone	3.1		1.80	1.36	1.32
9,10-Anthraquinone	13.9				

* $\sqrt{(h_2/h_1)} = 1.25$.

Since it was observed that only *p*-benzoquinone monoxime showed abnormally small diffusion currents at low pH's, these were investigated further by varying the height of the mercury reservoir as illustrated in Table V. These

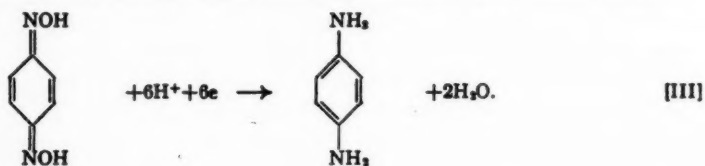
results indicate clearly that the wave at high pH's is diffusion-controlled for both 1,4-benzoquinone monoxime and 9,10-anthraquinone monoxime but only for 9,10-anthraquinone monoxime at low pH's. 1,4-Benzoquinone monoxime at low pH shows a reduction wave which is almost purely kinetic in nature, and this persists to the region where a double wave is observed. This proves that at low pH's the reduction of this compound must be preceded by a change at the surface of the electrode before reduction can take place. Since this reaction could not be the formation of the undissociated acids from the anion (pK for benzoquinone monoxime is about 6), it must involve tautomerization. This may involve the system *p*-nitrosophenol - benzoquinone monoxime or *p*-benzoquinone monoxime - *p*-benzoquinone nitron.

The diffusion currents have been found to be directly proportional to concentration in the range studied of 0.9 to $1.67 \times 10^{-4} M$.

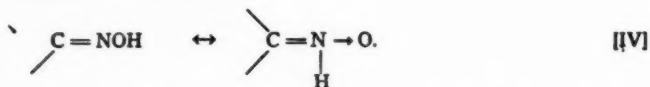
The half-wave potentials were subject to less variation with concentration than was the case with the dioximes. In the case of anthraquinone monoxime at pH 5.3 changing the concentration from $0.9 \times 10^{-4} M$ to $1.67 \times 10^{-4} M$ changed the half-wave potential by 0.01 v. In more acid solutions, and also in alkaline solutions, the half-wave potentials were much less dependent or not dependent at all on concentration.

DISCUSSION

The polarographic reduction of the oximes of aromatic ketones (5, 15) has been shown to involve four electrons and results in the production of the corresponding amine. Since the polarographic reduction of the quinone dioximes requires six electrons, the products of the reduction of these substances must be the corresponding diamines, according to equation [III]:



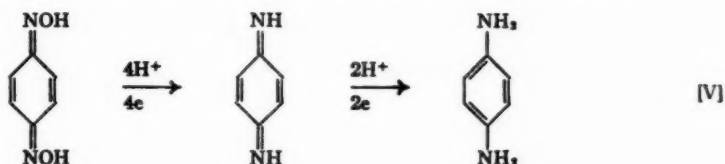
In the preceding section it has been shown that reduction in neutral solutions is stepwise. Since the lower wave is a kinetic wave, isomerization at the electrode before reduction must be postulated. As it has been pointed out, this must involve tautomerization and not simply re-formation of the undissociated oxime from the anion. Presumably this must involve some form of the classical nitron-oxime isomerization, equation [IV], postulated originally by Angeli (1) and applied to dioximes by Ponzio (12):



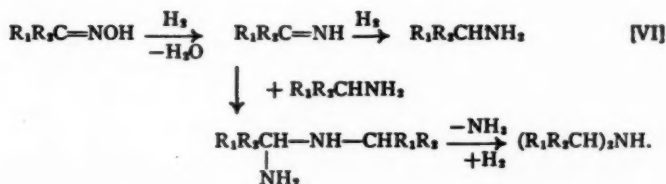
It is not possible from the results of this study to state which form is actually reduced at the electrode, but it is hoped that a consideration of these results

with infrared and ultraviolet spectra analyses currently in progress will elucidate this isomerism. In strongly alkaline solutions, the anion is stabilized by resonance and the molecule is reduced at a considerably higher potential.

The actual reduction probably proceeds according to equation [V]:



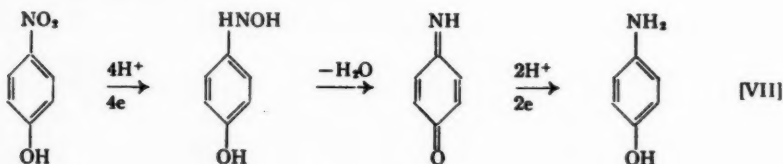
through the intermediate diimino compound. This mechanism is supported by the fact that the slope of the plot of E_1 vs. pH in acid solutions approximates 0.100, which corresponds to a critical step involving four H^+ and presumably four electrons. The results of catalytic and electrolytic reduction of various oximes has necessitated the hypothesis of a similar mechanism. These reductions result in the formation of mixtures of both primary and secondary amines. In order to explain this, von Braun (3) postulated similar imino intermediates which condense with the amine already produced. Elimination of ammonia and further hydrogenation results in the formation of the secondary amine according to equation [VI]:



As illustrated in Table III, the polarographic reduction of benzoquinone dioxime at a pH of 7.3 results in a single wave of about one-half the normal height. Since this is a kinetic wave whose height depends on a rate of isomerization, no conclusion can be drawn, at this pH, about the formation of final reduction products corresponding to the dihydroxylamine or the diimino compound. That is, the small wave height may be due entirely to slow isomerization of the dioxime, and only the normal reduction product—the diamine—may be produced.

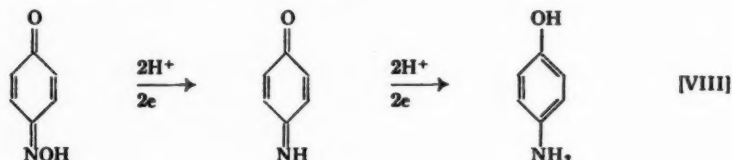
In all cases where diffusion-controlled waves were observed the reduction of quinone monoximes involves four electrons; hence the over-all reduction product must be the corresponding aminophenol over the entire pH range. On the other hand, the reduction of nitrosobenzene has been shown to stop at the phenylhydroxylamine stage in the pH range studied here. The polarographic reduction of nitrobenzene proceeds to phenylhydroxylamine in alkaline solution, and to aniline in acid solution. *p*-Nitrophenol is reduced stepwise at

nearly all pH values to *p*-aminophenol. In the case of *p*-nitrophenol these observations have been explained by the hypothesis of quinoidation (16), according to equation [VII]:



However, *p*-nitrosophenol (benzoquinone monoxime) is reduced in one step and at more positive potentials than *p*-nitrophenol. For *p*-nitrophenol, at pH 3, Astle and McConnell (2) report a stepwise reduction at $E_1 = -0.41$ and -0.86 v. whereas this investigation has shown a single step reduction at pH 3.9 of $E_1 = 0.04$ v. for benzoquinone monoxime. Furthermore, at pH 12, they found that E_1 was -0.93 v. and -1.57 v. for *p*-nitrophenol, whereas at pH 11.4 this investigation showed $E_1 = -0.88$ v. for benzoquinone monoxime.

These results indicate that the reduction of the monoximes does not involve the intermediate formation of *p*-hydroxyphenylhydroxylamine which would be expected during the reduction of *p*-nitrosophenol, but rather the reduction of the oxime according to equation [VIII]:



This mechanism is supported by the results of the reduction of the quinone dioximes and by the results of the chemical reduction of oximes. The fact that the wave for 1,4-benzoquinone monoxime at low pH's is a kinetic wave indicates that the oxime or other species actually reduced must form slowly at the electrode before reduction can take place. The other monoximes either do not need to rearrange before reduction, or else rearrange very rapidly. As discussed in the section on the dioximes, the possibility of the existence of nitron forms of the oximes must be considered. This point will require further investigation but the ultraviolet work of Ramart-Lucas (13) confirms the existence of three forms of benzoquinone monoxime in buffered solutions. These are probably nitrosophenol, benzoquinone monoxime, and the corresponding nitron.

Whereas the reductions of the quinone oximes are irreversible and no particular significance should be placed on the slope of the waves, it is interesting to compare the values obtained by plotting E_d vs. $\log [i/(i_d - i)]$. In alkaline solution no variation of the slope as a function of structure is obtained, but in acid solution the values obtained for the corresponding monoximes at pH 3.9 are: 1,4-benzoquinone 32 mv.; 1,2-naphthoquinone 52 mv.; 1,4-

naphthoquinone 58 mv.; and 9,10-anthraquinone 73 mv. The corresponding figures for the dioximes at pH 3.1 are 36 mv., 35 mv., 47 mv., and 69 mv., respectively. The values correspond to actual slopes that are much too low for the number of electrons involved in the reduction. However, it is noteworthy that the derivatives of benzoquinone have much steeper waves than the derivatives of anthraquinone. The derivatives of the two naphthoquinones have waves of intermediate slope. This, of course, is the order of aromaticity of the parent hydrocarbons, the oxidation potentials of the corresponding quinones, and, particularly, the order of conjugation between the functional groups in the oximes themselves.

Since the reactions are highly irreversible, it is not feasible to attach much significance to the actual half-wave potentials of the monoximes and dioximes and their relationship to the reduction potentials of the quinones. However, the fact that the half-wave potentials of the anthraquinone derivatives are at the more negative potentials, and those of benzoquinone derivatives are at more positive potentials, indicates that conjugation is the controlling factor. Since 1,2-naphthoquinone derivatives have potentials very close to those of the benzoquinone oximes, this would indicate a very high degree of conjugation due to proximity of the functional groups.

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THE METAL-SOLUTION SILVER ION EXCHANGE¹

BY I. I. TINGLEY,² I. H. S. HENDERSON,³ AND C. C. COFFIN⁴

ABSTRACT

The exchange of silver ions between silver nitrate solutions and surfaces of metallic silver was studied, using radioactive silver (Ag^{110} , 270 day half-life) as a tracer. Marked differences in behavior of surfaces prepared in different ways were observed. Crystalline (annealed and etched) surfaces exchanged rapidly to a depth of a few atomic layers, and about 80% of the acquired radioactivity was removed as quickly by exchange with inactive silver nitrate solution. Highly polished surfaces exchanged up to ten times as great an extent as the etched annealed surfaces, but required 40 hours' immersion to attain their maximum activity. The deactivation of polished surfaces by inactive solutions was inversely proportional to the period of immersion in active solution, with surfaces immersed for 17 hr. or more retaining all but 30% of their acquired activity. Abraded surfaces exchanged quickly and retained most of their activity, the extent of the exchange depending upon the ratio of "worked" to "unworked" material on the surface. Some evidence of comparatively rapid diffusion in the polish layers was obtained. The interior of cold-worked silver when exposed to the nitrate solution behaved similarly to abraded surfaces. Mechanisms for the behavior of these different types of surface are offered, and the data of other workers discussed.

INTRODUCTION

Experiments on the exchange of silver ions between silver metal surfaces and dilute solutions of silver nitrate were carried out in the Chemistry Department of Dalhousie University between 1948 and 1950. Brief reports on the earlier part of this work have been published (5, 26). While further work is necessary before the exchange mechanisms can be fully elucidated, it was felt that a presentation of these results and suggested mechanisms might be of value to others working in the field.

Excellent reviews of the published work on metal-metal ion exchanges have been made by Haïssinsky (13) and Simnad (23). In order to indicate the development of ideas about the mechanisms, however, a brief summary of certain investigations is given here.

The first published reports of metal-solution ion exchanges are those of Hevesy and Biltz (15). Using lead marked with thorium B, they observed a rapid exchange, extending to 1000 atomic layers, considering the surface to be perfectly flat. They postulated local currents on the surface to account for this exchange, and pointed out that the exchange between a layer of lead dioxide and a lead nitrate solution was much slower. This latter exchange approached much more nearly the ideal case of a "kinetic" exchange, according to their view. A lead sol did not show the rapid exchange with the solution that the massive lead surface did, and the authors explained this as due to the formation of an electrical double layer around each colloidal particle of lead.

¹Manuscript received in original form April 25, 1955, and as revised, October 4, 1955.

²Contribution from the Department of Chemistry, Dalhousie University, Halifax, Nova Scotia.

³Present address: Nuclear Metallurgy Division, Department of Mines and Technical Surveys, c/o Metallurgy Branch, Atomic Energy of Canada, Ltd., Chalk River, Ont.

⁴Present address: Chemistry Department, Canadian Services College, Royal Roads, Victoria, B.C.

⁵Formerly Harry Shirreff Professor of Chemical Research and Head of the Department of Chemistry, Dalhousie University, Halifax, N.S.; Dr. Coffin died January 12, 1954.

Erbacher was the first to study the effect of surface treatment upon the metal-solution exchange (8). Mechanical abrasion with emery or sandpaper caused on some metals multilayer exchange due to local electrolytic cells, he explained, but with other metals, or after passivation of the cells in certain conditions, only monolayer exchange took place. He also studied similar exchanges between metals and "nobler" metal ions, and used the metallic exchange to measure the actual area of metal surfaces. For silver he found that a polished surface had 1.72 times the area of the surface as measured ordinarily, while coarse- and fine-sandpapered surfaces had 2.49 and 2.53 times the measured areas, respectively.

With abraded silver surfaces (polished with crocus cloth) Rollin observed an exchange involving 150 atomic layers with silver nitrate solution (22). Gold and platinum surfaces also exchanged to a depth of 100 atomic layers with silver nitrate solution.

Cottin and Do Carma Anta carried out experiments with silver metal powder and 0.2 *M* silver nitrate solution. Some of the powder was prepared by chemical reduction of silver nitrate solution by NaH_2PO_2 and some by electrolytic deposition from a 15% silver nitrate solution. The exchange with the metal prepared by electrolysis was found to involve 30 atomic layers compared with 7500 atomic layers for the silver prepared by chemical reduction, in 20 hr. For short times (a few minutes) at 100° C., the exchange involved 20 layers with electrolytic and 1000 atomic layers with chemically reduced silver. The exchange increased with temperature, and decreased after pretreatment with inactive silver nitrate solution. After exchange of long duration, the structure of the powder of chemical origin was found to have modified; it recrystallized in contact with the solution (14).

Simnad and Ruder used radioactive cobalt in solution and surfaces of various metals in both oxygen-containing and oxygen-free solutions (24). They were the first to publish autoradiographs, showing that when an abraded surface was exposed, the radioactive cobalt was deposited on the cathodic (unworked) areas.

Gerischer and Vielstich found a rapid initial exchange which varied in extent with the surface treatment, but was to a depth of 20 atomic layers with crystalline silver. When specimens were immersed for long periods of time, they found a second slower increase in the radioactivity of the metal, and explained this as due to diffusion into the metal lattice. The process was considered to consist of three steps: (a) the diffusion through the solution to the surface, (b) the discharge of ions at the boundary and their entry into the "exchange-layer", and (c) the diffusion into the solid lattice (11).

Baerg and Winkler found that abraded foils, which had 15 times the planar area, as measured by the Bowden-Rideal method, exchanged in one hour to a depth of 30 atomic layers with a 3×10^{-4} *N* silver nitrate solution. When equilibrated with inactive silver nitrate solution of the same concentration for 300 hr. or more, they exchanged with the radioactive solution to a depth of 15 atomic layers. When foils of the same metal were etched with 7 *N* HNO_3 , they gave Bowden-Rideal areas of 8 times planar, but exchanged to a depth

of only 2.5 atomic layers, and the exchange was unaffected by inactive equilibration. Fifty to sixty per cent of the acquired radioactivity on both types of surface was subsequently removable by exchange with inactive silver nitrate solution (1).

In kinetic studies on etched surfaces, Baerg and Winkler used the equation $-2.3 \log F = kt$, where $F = (x_3 - x)/x_3$ for the forward equation (inactive surface, radioactive solution) and $F = (x - x_3)/(x_0 - x_3)$ for the reverse reaction (radioactive surface, inactive solution). x is the radioactivity on the surface at time t , x_3 is the value of x at the end of three hours, and x_0 is the initial (zero time) activity for the reverse exchange; k is a proportionality constant. The lines obtained were segmented, with straight portions, except for the reverse exchange from electrodeposited adsorbed ions, which gave a definite curvature. In the earlier portions, the lines for forward and reverse exchanges coincided; after about 12 min., however, the reverse rate was lower, and the slope of its line less. According to the authors, the segmented appearance of the graphs indicates several different rates of reaction and disclosed the heterogeneous character of the metal surface. The curved plot indicated a surface structure of a completely heterogeneous character and suggested random, "out-of-lattice" deposition of the ions. They explained the heterogeneous character of the other surfaces to be due to crystal faces of different orientation, each of which exchanges at a separate rate.

EXPERIMENTAL

A. Apparatus

In the work described below, silver metal surfaces prepared in various ways, as indicated, were exposed to 0.1 *N* or 0.005 *N* silver nitrate solutions containing radioactive silver (Ag^{110} , 270-day half life) and to 0.1 *N* and 0.005 *N* inactive silver nitrate solutions, with a view to determining the effect of surface treatment upon the exchange taking place between silver metal and its ions in nitrate solution.

The solutions used were as follows:

- (1) 0.1 *N* silver nitrate solution, containing Ag^{110} and giving 4×10^4 c.p.m. per ml. when evaporated on a 1-in. in diameter planchet.
- (2) 0.005 *N* silver nitrate solution containing Ag^{110} and giving 1×10^6 c.p.m. per ml. This solution had a pH of 6.2.
- (3) Inactive 0.1 *N* silver nitrate solution.
- (4) Inactive 0.005 *N* silver nitrate solution, with a pH of 6.2.

The radioactive solutions were prepared by dissolving silver foil of high specific activity in nitric acid and evaporating the solution just to dryness. The resulting silver nitrate crystals were taken up in distilled water, the solution re-evaporated, the crystals redissolved in distilled water and made up to the required volumes. Inactive solution No. 3 was prepared in the same way, using inactive foil, while solution No. 4 was prepared by dissolving Merck

reagent grade silver nitrate. Isotopic dilution of the radioactive solutions, when necessary, was carried out by the addition of inactive silver nitrate of the same concentration.

The silver metal was obtained from Johnson, Matthey, and Mallory in the form of 0.12 mm. cold-rolled foil and $\frac{3}{8}$ in. in diameter rods. The specimens for the exchange experiments were prepared as $\frac{3}{8}$ in. disks or $\frac{3}{8}$ in. squares of the silver foil, or, in the later experiments, to obtain more reproducible surfaces, $\frac{3}{16}$ in. slugs cut from the silver rods. The circular surfaces thus had areas of 2.8 cm.², and the square ones 3.63 cm.²

Unless otherwise stated, the silver was annealed before each experiment for at least two hours in a muffle furnace at 850° to 950° C. in order to obtain a reproducible starting point for the preparation of each specimen. This annealing produced grains up to 3 mm. in diameter in silver which had been severely cold-worked previously. Surfaces described as "annealed, etched" were prepared by etching specimens of annealed silver with 35% nitric acid, and surfaces described as "emered" were annealed specimens rubbed with 00 metallographic polishing paper.

Several silver slugs were electrolytically polished. The polishing cell consisted of a 150-ml. beaker containing phosphoric acid (specific gravity 1.7) and a cylindrical silver foil cathode held coaxially with the anode, the slug to be polished. Electrical contact and support for the anode was a 1/16 in. platinum rod threaded into the edge of the slug, and insulated from the solution by a coating of paraffin wax. With a current density of about 50 ma. per sq. cm., electrolytic polishing of the anode took place, producing a bright crystalline surface, with individual crystals well defined in specimens of large grain size.

Silver foil was polished as a strip 6 in. by 1½ in. by hand polishing or on a low-speed polisher, before it was cut into disks or squares. Polishing was carried out by hand using a water suspension of levigated alumina and chamois skin, and on the polisher by affixing the silver strip to a smooth, curved block of wood which was held against a velvet lap continually moistened with a water suspension of levigated alumina. Silver metal slugs were polished by the procedure suggested by Desch (6), using three grades of metallographic polishing paper followed by a smoothing of the surface on a wax lap with levigated alumina. The final polishing was carried out on the low-speed polisher using Linde "B" (alumina) on a "Gamal" lap. The flow of material reported by Beilby (3) in final polishing was observed under a low-power microscope, polishing being discontinued when surface scratches were no longer visible. After polishing, the surfaces were rinsed with water and then with alcohol. In some instances a solution of potassium hydroxide in alcohol was used to remove grease film, followed by distilled water. This treatment had no observable effect on the surface of the metal or on its behavior when exposed to silver nitrate solution.

For exposure to the silver nitrate solution, silver foils were cemented to a picene wax block, and the block suspended in a stirred electrolytic beaker containing 100 ml. of solution. Silver slugs were individually mounted on the

flattened ends of 6 mm. glass rods by means of picene, with the edges of the slugs and the portion of the mounting rods in contact with the solution carefully painted with molten paraffin wax. Seven such specimens mounted on glass rods were exposed to the solution simultaneously, the upper ends of the rods being retained in fuse clips on a circular holder as shown in Fig. 1.

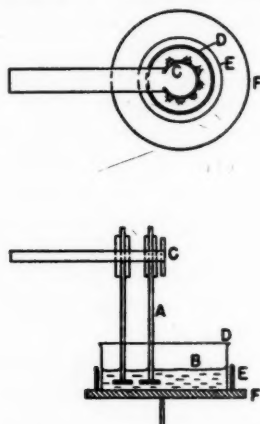


FIG. 1. Slug holder and stirrer assembly. A. Glass rod and silver slug. B. Silver nitrate solution. C. Slug holder with fuse clips. D. 10-cm. crystallizing dish. E. Steel guard ring. F. Phonograph turntable.

It was concluded after runs made both with and without nitrogen bubbling through the solution that the exchange phenomena discussed below were not dependent upon the presence or absence of oxygen. Stirring of the solution at a uniform rate was achieved by revolving the cells containing solution at 78 r.p.m. on a phonograph turntable, the silver specimens being held stationary.

The pH measurements on silver nitrate solutions were made with the system illustrated in Fig. 2, which consisted of a glass electrode, a calomel electrode,

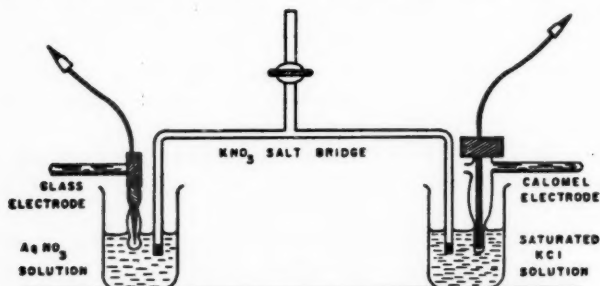


FIG. 2. Apparatus for pH measurement on AgNO_3 solutions.

a salt bridge containing 2 *N* potassium nitrate solution, and a Beckman Model G pH meter. The meter was standardized against buffer solution of pH 7.

After exposure to solution, specimens were rinsed in distilled water, cleaned with boiling benzene and then with detergent (Alconox), and the radioactivity was determined using an end-window β - γ counter in a conventional setup, with the counter tube shielded in a lead "castle". At least 1000 counts were taken from each sample, so the statistical error limit in the counts was 6%. The counts were corrected for day to day fluctuation of the counter efficiency, and for decay, by comparison with a standard Ag^{110} source.

B. Experimental Results

From their behavior toward silver nitrate solutions, the different silver surfaces were classified as crystalline, polished, and "mixed". A "mixed" surface is defined as a surface prepared by scratching, grinding, or partially polishing an annealed specimen, so that some unworked metal is left exposed along with the worked portions.

A number of runs established a marked difference between polished and crystalline (etched) surfaces in the uptake of radioactivity from the solution. Crystalline surfaces acquired very quickly an activity of 10 to 20 c.p.m. from solution No. 1, and this did not increase during immersion up to nearly 90 hr. in the solution, while polished disks acquired radioactivity in a regularly increasing amount until a maximum of about 200 c.p.m. was reached at about 40 hr. After 24 hr. in the solution about 85% of the maximum radioactivity was obtained. Values for a typical run are plotted in Fig. 3.

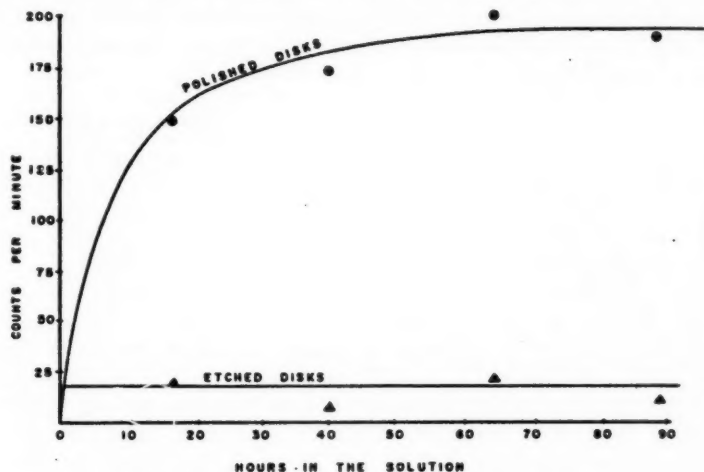


FIG. 3. Activity uptake of etched and polished disks.

Considering the surface of the disks to be perfectly flat, it was calculated that the maximum uptake of radioactivity by the etched and polished surfaces amounted to penetrations of 11 and 110 atomic layers, respectively, i.e., that the amount of silver which had transferred from the solution to the metal surfaces was sufficient to make up these numbers of layers. The value for the

polished surface compared well with the 100 to 150 atomic layers' penetration found by Rollin for silver surfaces, while that for the etched surfaces is comparable to the figures of 20 and 30 atomic layers found by Do Carmo Anta and Cottin for electrodeposited silver, which was certainly crystalline, and to the value of 20 atomic layers found by Gerischer and Vielstich for surfaces etched with nitric acid or electrodeposited from solution.

Using solution No. 2, with a higher specific activity and much lower concentration, a similar pair of curves was obtained, the maximum for the polished surfaces being only five times as high as that for the etched ones, however. There is some uncertainty regarding the number of layers penetrated, due to the fact that the solution radioactivity was determined by evaporating an aliquot on a 1-in.-in-diameter planchet, while the specimens used in the exchange were $\frac{1}{4}$ in. squares. The difference in counting efficiency might be as much as 30%. Neglecting this factor, the penetration with solution No. 2 amounted to only 3.5 atomic layers for etched surfaces and 17 atomic layers for polished surfaces. This value for crystalline surfaces agrees fairly well with those of Baerg and Winkler, who used a solution of 3×10^{-4} *N* concentration, and would seem to indicate that the depth of the exchange depends to some extent upon the concentration of the solution. Electropolished surfaces prepared from annealed metal without prior abrasion took up approximately the same amount of radioactivity as the etched surfaces, while if the surface was emiered before electropolishing the uptake was two or three times as great.

When the mixed surfaces produced by etching unannealed foil were exposed to the solution along with polished surfaces, the radioactivities acquired by both types of surface were almost identical, as shown by Fig. 4.

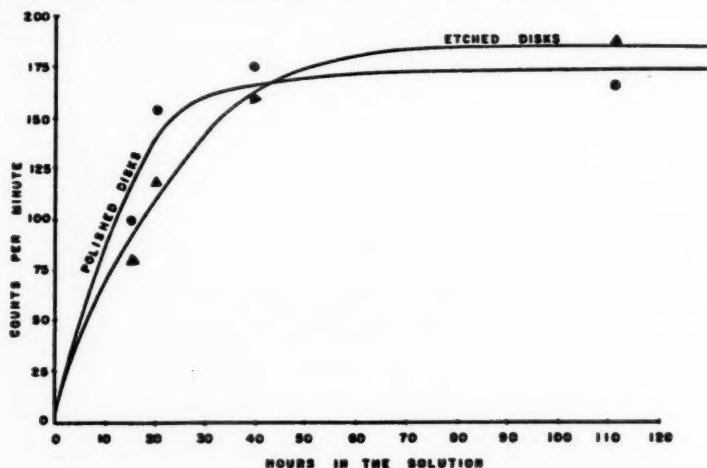


FIG. 4. Activity uptake of unannealed etched and polished disks.

To determine how quickly the radioactivity was acquired upon immersion of the disks in the solution, etched and polished disks were exposed to solution

No. 1 for instant dips, 10 sec., 1 min., 15 min., 30 min., and 60 min. The results are plotted in Fig. 5. Each count represents a different specimen and

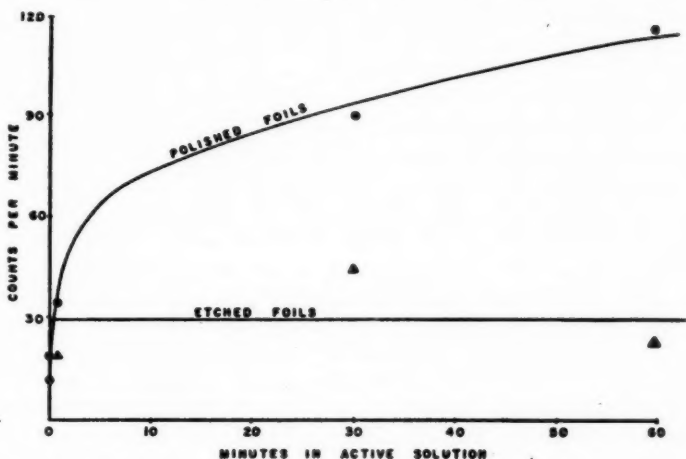


FIG. 5. Behavior of etched and polished surfaces immersed for short periods in silver nitrate solution.

with the etched ones the values were random with respect to time, with the instant dip giving 20 c.p.m. Polished surfaces, though apparently slower starting (13 c.p.m. after an instant dip), continually increased their radioactivity, but at an ever-slower rate, up to the end of the test period.

Experiments with solution No. 2 gave very similar results, to which reference will be made later.

In attempting to show that an electric potential difference existed between the amorphous polish material and the crystalline metal, experiments were carried out in which disks of the same size were connected by a strip of the same foil, the whole dumbbell piece being cut out from a polished strip at one time. One disk of the dumbbell was etched, the other left polished. The piece was placed on the wax block and the connection waxed over, so that the two disks were connected electrically outside the solution. It was thought that if a potential difference existed between the two disks, the polished one would go into solution to some extent, while an equivalent quantity of ions would plate out on the crystalline disk. Compared with unconnected disks in the same solution for the same time, the polished connected disk would acquire less radioactivity and the etched connected one more activity than the respective unconnected ones. The results of many such runs were inconclusive, however, as the effect seemed to be indicated sometimes and in other cases was definitely absent. Modifications on the experimental arrangement were tried, but always the results were inconclusive.

Other workers have observed that the exchange between silver metal and silver ions in solution was diminished by pretreatment of the silver surface

by exposing it to inactive silver nitrate solution (1, 8, 11, 14), although Haïnsky and his collaborators found the opposite effect with some metals (14). Polished and etched disks were exposed to inactive solution No. 3 for 19 hr., and then put into radioactive solution No. 1, one pair for an instant, and two other pairs for 30 and 90 min., respectively. The counts obtained on the polished disks were 17, 132, and 168 c.p.m., respectively, while the results for the etched disks were 9, 26, and 36 c.p.m. Later experiments with both foils and slugs in radioactive solution No. 2, after pretreatment for times of 1 min., 5 min., 1 hr., and 17 hr. in inactive solution No. 4, showed that the uptake of activity by both crystalline and polished surfaces was unaffected by pretreatment with inactive solution of nearly neutral pH (6.2). However, using

TABLE I
EFFECT OF ACIDITY OF PRETREATING SOLUTION ON ACTIVITY UPTAKE

Surface	Activity (c.p.m.)	
No pretreatment	100	130 (two disks)
Pretreated with solution of pH 5.4	140	115
Pretreated with solution of pH 0.3	230	250

crystalline silver slugs and inactive 0.005 *N* silver nitrate solution with its pH adjusted, the results found in Table I were obtained after one minute each in the inactive solution and in radioactive solution No. 2. It thus appears that the increase in exchange found with solution No. 1 after pretreatment with solution No. 3 may have been a pH effect. It may also have been just the result of a different degree of polish.

Rollin found that the pretreatment of an inactive silver surface with sodium nitrate solution increased its radioactivity uptake by a factor of 10. When

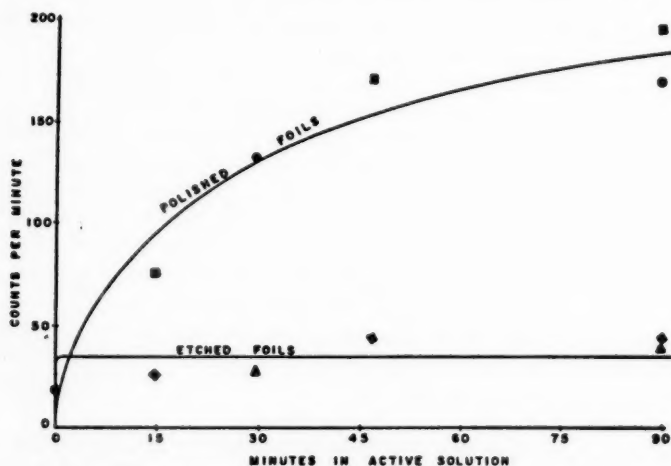


FIG. 6. Effect of pretreatment with inactive solutions upon exchange.

this was tried by the authors, the results agreed very well with those obtained in the silver nitrate pretreatment, the increase in activity uptake being about 1.5 times for polished surfaces, rather than 10 times, and no change with etched surfaces. More careful experiments should be made to check the effect of pretreatment on the different surfaces. The results of these experiments are plotted in Fig. 6, which should be compared with Fig. 5.

Besides the observation that unannealed foil when etched gave a less obviously crystalline surface, which took up considerable activity from the solution, the effect of cold-working on the properties of the interior of the metal was shown by the following experiments: Two pieces of annealed foil, of the same size, were cut out, and one was pounded with a hammer on an anvil for some time. The two pieces were then set on the wax block, etched, and put into the radioactive solution No. 1. After five hours they were removed and counted. The results were: 98 c.p.m. for the pounded piece, and 17 c.p.m. for the unpounded one. Silver slugs, $\frac{1}{8}$ in. thick, were placed on a steel block and pounded out to a thickness of about $\frac{3}{64}$ in. by a single 2000 p.s.i. blow from an electric hammer. After etching with nitric acid, some of these slugs were annealed, and then they were all exposed to the radioactive solution. The unannealed slugs took up three to five times as much radioactivity as the annealed ones.

In an attempt to get a more quantitative idea of the effect of cold working, three pieces of annealed foil, about 2 cm. square, were treated as follows: While it was held between two blocks of wood, the piece was bent through a right angle in each direction for a number of times, and then shifted and bent again at a different place. The pieces were bent in this way at four lines along one dimension, and at four lines along the other dimension, one piece for 4 times, a second for 8 times, and a third for 16 times. (Bending more than 18 times resulted in fracture of the metal.) These pieces were then put on the block along with an unworked piece of the same foil, all four pieces were etched and put into radioactive solution No. 1 for 22 hr. Upon counting, the results were: for the unworked piece, 44 c.p.m.; the one worked 4 times, 56 c.p.m.; 8 times, 53 c.p.m.; and 16 times, 60 c.p.m. Thus, although there was little difference between working the pieces 4 times or 16 times in this way, the difference between worked and unworked appears real. It must be remembered also that etching with the acid undoubtedly removes more of the worked material than the unworked, and so the difference in behavior is probably greater than was found.

To determine how the ratio of "vitreous" or worked metal to crystalline metal affected the uptake of radioactivity, the following experiments were performed.

From a sheet of annealed, etched foil, four disks were prepared, one being polished with wet, fine alumina for 6 sec., a second for 60 sec., a third for 600 sec., and the fourth left unpolished. After being held in the active solution No. 1 for one minute, the disks showed radioactivity as follows: No. 1, (polished 6 sec.) 36 c.p.m.; No. 2 (polished 60 sec.) 111 c.p.m.; No. 3 (polished 600 sec.) 32 c.p.m.; and No. 4 (unpolished) 23 c.p.m. After being in the solution a

further nine minutes, the disks counted: No. 1, 47 c.p.m.; No. 2, 168 c.p.m.; No. 3, 73 c.p.m.; and No. 4, 28 c.p.m. When returned to the radioactive solution for further periods, the disks increased their radioactivities regularly, with the magnitudes of the increases being in the order No. 2, No. 3, No. 1, and No. 4, until at 17 hours' total exposure to the solution the counts were No. 1, 118 c.p.m.; No. 2, 392 c.p.m.; No. 3, 214 c.p.m.; and No. 4, 67 c.p.m.

When the disks were put into inactive solution No. 3 for the same periods of time, their radioactivities were lost in a similar manner, except that the most highly polished disk retained its radioactivity through the one minute period, while all the others lost considerably. After 17 hr. in the inactive solution the counts were No. 1, 72 c.p.m.; No. 2, 248 c.p.m.; No. 3, 175 c.p.m.; and No. 4, 37 c.p.m.

These results are plotted in Fig. 7.

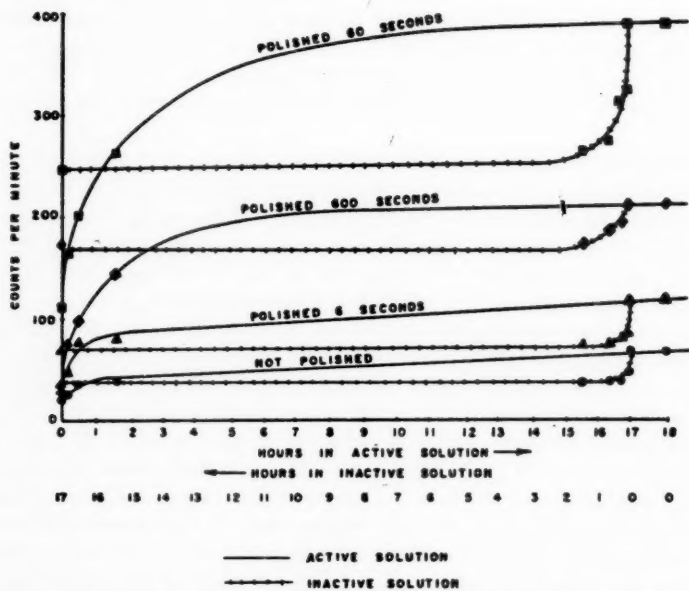


FIG. 7. Effect of vitreous to crystalline ratio upon activity uptake of surfaces.

Two more runs were carried out, in which the numbers of strokes with the polishing chamois were counted, and the foils exposed to solution No. 2 for 17 hr. The results are given in Table II. Another run was made with annealed slugs polished for different times on the Buehler polisher, and the surfaces exposed to solution No. 2 for 17½ hr. The data are given in Table III.

An alternative to the Geiger counter in detecting radioactivity is the method of autoradiography, which has the advantage of indicating the location of the activity more precisely. This would be particularly useful in the case of "mixed" surfaces, it was thought. Autoradiographs of etched specimens of

TABLE II

Amount of polishing		Activity uptake (c.p.m.)	
1st Run	2nd Run	1st Run	2nd Run
2 strokes	2 strokes	440	1673
4 strokes	21 strokes	846	2100
16 strokes	24 strokes	1520	2760
48 strokes	51 strokes	4170	5400
Good polish	Good polish	3250	4320
High polish	High polish	2870	3985
None	None	240	510
None	None	260	315

TABLE III

Time on polishing lap	Activity uptake (c.p.m.)
None	570
1 sec. (low speed)	1620
5 sec. (low speed)	2430
5 sec. (high speed)	2430
20 sec. (high speed)	2100
50 sec. (high speed)	1910
160 sec. (high speed)	1830

unannealed foil having smooth streaks through the rougher crystalline surface, which had acquired a small amount of radioactivity in active solution No. 1, were made by placing the specimens down on pieces of dental X-ray film, and leaving them in the dark for periods of time necessary to get clear images.

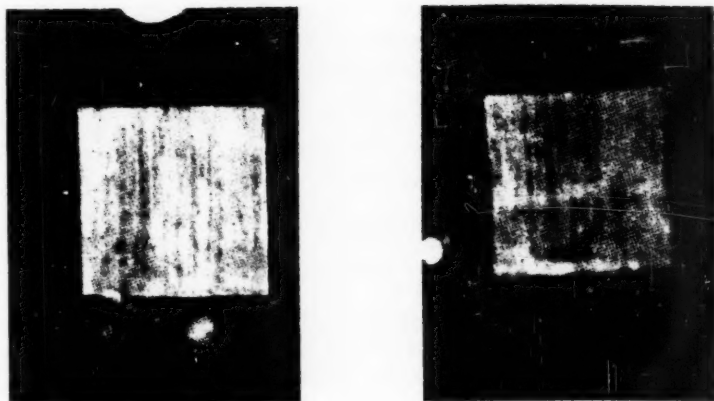


FIG. 8. Photograph and autoradiograph of unannealed etched silver surface. The picture on the left was taken with a camera, with the light placed so that the smooth lustrous streaks were in the shadows of the rougher, more crystalline portions. The autoradiograph, at the right, shows that the radioactivity was concentrated in these crystalline, unworked, cathodic portions of the metal surface.

When the negatives were developed and compared with the silver surfaces, it was seen that the radioactivity was concentrated on the crystalline (unworked) portions of the surface. This result is similar to that obtained by Simnad and Ruder in their studies with cobalt surfaces and radioactive cobalt solutions (24). Fig. 8 shows a print from the autoradiograph and one from a photograph of the same surface. The smooth streaks were in the shadows of the rougher crystalline portions of the surface when the photograph was taken, and so appear darker in the print. In the autoradiograph they also appear darker, but for the reason that the radioactivity was concentrated on the rougher, crystalline portions, and affected the negative accordingly.

Pieces having surfaces consisting of alternate polished and etched strips were made up, the strips being about 2 mm. wide. These were immersed in radioactive solution No. 1 for several hours, and autoradiographs made of them. These showed that in general the activity was concentrated in the polished strips. However, one etched strip was almost completely active, others were much narrower on the autoradiographs than on the metal pieces, and when the widths of the etched strips on the foils and the widths of the light strips on the films were measured with a micromicrometer, it was found that all light strips on the negatives were narrower than the actual strips on the metal, the differences in width at various positions along the strips varying from 2 to 64%. This was not due to film shrinkage, as the total width of the film image was the same as that of the piece of metal. In these pieces the etched strips were really furrows, being at a lower level than the polished strips, due to the dissolving of the metal during the etching. Considerable radioactivity was probably acquired by the banks of these furrows, since there crystalline metal existed in closest contact with the polish material. Radioactive emanations from these banks would affect the film in such a way that the light streaks corresponding to the etched strips would be narrower than the strips on the metal pieces. This is diagrammed in Fig. 9.

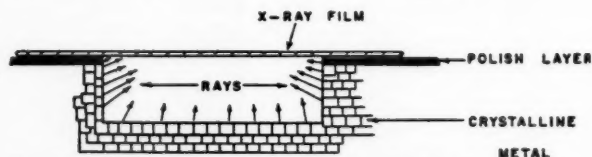


FIG. 9. Diagram of effect of etched and polished strips on film.

The experiments to determine the effect of the ratio of annealed to worked metal indicated that some 20% to 40% of the radioactivity acquired by the silver surfaces after 17 hours' exposure to radioactive solution No. 1 was lost when the surfaces were immersed for an equal period in inactive solution No. 3. The most crystalline surfaces lost the greatest percentage and the most highly polished one the least. Other experiments with well-annealed crystalline surfaces had indicated that such surfaces lost little or none of their acquired radioactivity (5), but the low radioactivity taken up made the results highly uncertain. The deactivation phenomena were investigated further, with the more active solution, and the results appear in Table IV.

TABLE IV

Type of surface	Type of specimen	Time in active solution No. 2	Time in inactive solution No. 4	Per cent loss
Crystalline	Foil	1 sec.	17 hr.	78
		5 sec.	17 hr.	80
		15 sec.	17 hr.	79
		1 min.	17 hr.	86
		17 hr.	17 hr.	75
		1 min.	1 min.	69
Polished	Slug	19 hr.	40 hr.	75
		1 min.	1 min.	74
	Foil	17 hr.	17 hr.	30
		5 min.	17½ hr.	57
	Slug	15 min.	17½ hr.	47
		1 hr.	17½ hr.	60
		4½ hr.	17½ hr.	44
		40 hr.	40 hr.	25
Partially polished	Foil	17 hr.	1 hr.	8
		17 hr.	3 hr.	6
		17 hr.	7 hr.	5
		17 hr.	24 hr.	8
	Slug	17½ hr.	17½ hr.	33
Emeried	Slug	17 hr.	17 hr.	21
		40 hr.	40 hr.	6

These results show that crystalline surfaces rapidly lost from 70% to 90% of the activity they had taken up from radioactive silver nitrate solutions, while polished surfaces which had been in the radioactive solution for at least

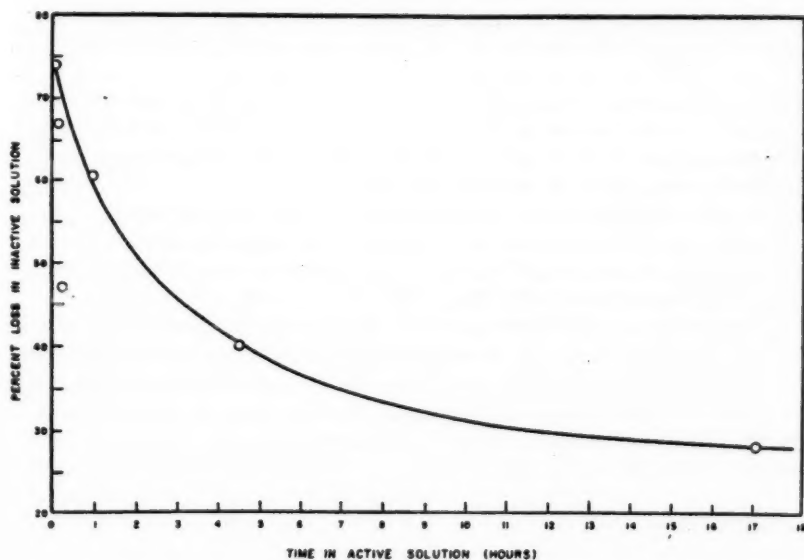


FIG. 10. Relation between deactivation of polished surface and time in active solution.

17 hr. lost 30% of their radioactivity in inactive silver nitrate solution. The radioactivity lost by polished surfaces in inactive solution was dependent on the time they had been in contact with the radioactive solution. This is shown graphically in Fig. 10. Partially polished foils and emiered surfaces lost the least, 5% to 20%.

The gradual uptake of activity by a polished surface could be nicely explained if atoms which entered the surface layer in the exchange process, including the radioactive atoms by which the exchange was detected, gradually diffused into the polish layer, to be replaced by other atoms both from the metal and from the solution. Diffusion in crystalline silver at room temperature is doubtless very slow (2), but in the disordered, amorphous polish layer it might be thousands of times as rapid as it is along grain boundaries (16). In this way the radioactivity of the metal would increase until the number of radioactive ions entering its surface equalled the number of active atoms re-entering the solution from the surface. In a search for evidence of such diffusion, silver disks which had been activated in an early run were recounted after 228 days. The original radioactivities of two such pieces had been 197 c.p.m. each, and after this lapse of time they counted 92 and 80 c.p.m., respectively, the decrease being accountable by the decay of Ag^{110} . The two disks were immersed in inactive solution for one and one-half hours, which according to previous experiments should have removed 30% of their radioactivity. On counting, however, the results were 97 and 85 c.p.m., respectively, which being within the statistical error limits of the previous counts, indicated that no radioactivity had been lost. To confirm that exchange was still taking place, the two disks were stirred in radioactive solution No. 1 for three hours, whereupon their activities increased to 200 and 210 c.p.m., respectively. Put back into inactive solution for 16 hr., they lost radioactivity to 150 and 148 c.p.m.; returned to the radioactive solution, after 18 hr. they gave 218 and 247 c.p.m.; and after a further 19 hr. in inactive solution 166 and 177 c.p.m. It was apparent that exchange was still going on, but as with new disks, after each exchange period some activity was retained in the foil and could not be removed by exchange with inactive solution.

To see if the original activity had penetrated to the crystalline interior, one of the disks was etched with 4 *N* nitric acid until the polish layer was removed. Upon counting, it gave only 4 c.p.m., which showed that practically all the radioactivity was removed with the polish.

Two more disks of the same age were counted, giving 75 and 77 c.p.m.; these were compared with two disks activated only a short time previously, which had radioactivities of 169 and 176 c.p.m. The old disks were stirred for three hours in inactive solution, and upon counting gave 74 and 78 c.p.m., while the new disks were put for five hours into radioactive solution, after which they gave 244 c.p.m. each. All four disks were then held for 15 sec. in 3.5 *N* nitric acid; no etching of the polish was visible after this. However, after counting, the new disks were seen to have 219 c.p.m. each, and the old ones 70 and 74 c.p.m. The radioactivities found after further periods in the acid are listed in Table V.

TABLE V

Total time in acid	Old disks (c.p.m.)		New disks (c.p.m.)	
0 sec.	74	78	244	244
15 sec.	70	74	219	219
30 sec.	70	73	218	206
90 sec.	68	63	173	196
450 sec.	38	52	143	162
630 sec.	26	47	87	122

After 450 sec. in the acid, the surface of the polished disks was just beginning to lose its mirror-like finish, while the activities had been cut down 33½% to 49% on all disks. It took 90 sec. with the old disks before appreciable removal of activity began, however, while with the new disks effective removal began at once. This would indicate that the penetration of the polish layer by radioactive atoms was only to a small depth for the most part, but that the radioactive atoms diffused into the polish layer with time, so that they were removed from the surface layers where exchange took place.

To determine whether the behavior of the polish layer was changed by heating, pairs of polished foils were heated at temperatures and for times indicated in Table VI before they were placed in solution No. 1 for 17 hr. Micro-

TABLE VI

Duration of heating	Temperature	Activity taken up (c.p.m.)	
None	25° C.	106	110
17 hr.	450° C.	29	76
17 hr.	540° C.	30	25
17 hr.	850° C.	30	25

scopic examination of the above surfaces before activation revealed that crystals were commencing to form in the polished surfaces of all the heated foils, suggesting that annealing of silver can be carried out at quite low temperatures. The data of Table VI confirm this, showing that the heated foils took up radioactivities comparable to those taken up by annealed foils.

Four highly polished silver slugs were heated to 850° C. for different times and then immersed in solution No. 2. After heating, the surfaces of the slugs still had a mirror finish. Table VII shows that heating to 850° C. for short times causes polished surfaces to revert to crystalline behavior with respect to the exchange with silver nitrate solution.

TABLE VII

Duration of heating at 850° C.	Time in solution No. 2	Activity (c.p.m.)
1 min.	17 hr.	1630
5 min.	44 hr.	1020
10 min.	17 hr.	350
45 min.	17 hr.	490

MISCELLANEOUS EXPERIMENTAL DATA

It was thought that if the polish layer was "vitreous" or, in effect, an under-cooled liquid, the behavior of a silver amalgam would be similar. Four polished silver disks were placed on the wax block, and their surfaces amalgamated. The block was immersed in active solution No. 1 for one hour, and then one disk was removed. The disks were all covered with crystals, unevenly deposited, some of which were so loose that they washed off while the block was being rinsed with water. After a further two hours in the solution, a second disk was removed; its surface was as crystalline as if etched with nitric acid. Upon counting, both disks gave more than 9000 c.p.m., and it was concluded that the mercury was displacing silver from the solution.

Two "dumbbell" pieces, or connected pairs of disks, one of each pair polished, the other etched, were put into the same solution that was used in the experiment with the amalgamated disks. One was removed after $17\frac{1}{2}$ hr., and the two disks separated and counted. The etched disk had an activity of 1228 c.p.m., and the polished one 145 c.p.m. After a further $23\frac{1}{2}$ hr., the other pair was removed and counted, the results obtained being 1156 c.p.m. for the etched disk and 257 c.p.m. for the polished. To check this behavior, two more connected pairs and two separated pairs of disks were immersed in the same solution. After two hours, a pair of connected and a pair of unconnected disks were taken off and counted; the results were: etched connected, 161 c.p.m.; polished connected, 39 c.p.m.; etched unconnected, 438 c.p.m.; polished unconnected, 31 c.p.m. After another 20 hr., the remaining pieces showed the following radioactivities: etched connected, 891 c.p.m.; polished connected, 91 c.p.m.; etched unconnected, 649 c.p.m.; polished unconnected, 95 c.p.m. The abnormally high activity taken up by all etched disks, connected or unconnected, since the mercury was put into the solution, indicated that the mercury ions were interfering with the silver ion exchange.

Rollin introduced gold and platinum foils into the radioactive silver nitrate solution, and observed radioactivities taken up by the foils amounting to a penetration of 100 atomic layers. To check this, two gold and two platinum disks were annealed for 24 hr. at $900^{\circ}\text{C}.$, etched with aqua regia, placed on the wax block, and one of each polished with wet alumina. (The platinum foil was so thin that not much pressure could be used in the polishing.) After immersion in radioactive solution No. 1 for 21 hr., the disks showed the following radioactivities: polished gold, 100 c.p.m.; etched gold, 20 c.p.m.; polished and etched platinum, 10 c.p.m. each. Examined under the microscope, the polished platinum disk showed a very crystalline surface. The counts obtained from the gold pieces seem to indicate that exchange takes place between gold metal and silver ions in silver nitrate solution.

The electrochemical behavior of polished and crystalline substrates of silver was investigated in the following manner: silver from a silver nitrate solution containing Ag^{110} was electroplated on polished and crystalline substrates, and was removed by making the electroplated surface the anode in the plating cell. The electrodes were silver slugs $\frac{3}{4}$ in. in diameter and $\frac{1}{8}$ in. thick. These were supported in the cell by $1/16$ in. platinum rods which also served as

electrical contact with the slugs. The plating bath was 0.002 *N* silver nitrate having a radioactivity of 1.5×10^4 c.p.m. per ml. In these experiments, sufficient silver was plated on the slugs at about 0.3 ma. to give them an activity of approximately 12,000 c.p.m., representing a charge transfer during plating of about 0.09 coulombs. Silver was removed from the slugs by reversing the polarity of the cell and passing about 0.03 coulombs per increment. To determine the amount of silver removed, a coulometer containing the same silver nitrate solution was placed in series with the removal cell, the coulometer cathode and removal cell anode being counted between increments. Activities were corrected for coincidence losses using the manufacturer's statement of the counter resolving time. The coulometer cathode was replaced by an inactive cathode when its activity exceeded 12,000 c.p.m., in order to reduce counting errors. The data are tabulated in Table VIII.

TABLE VIII

Run No.	Substrate type	Anode activity, %	Coulometer cathode activity (as % original anode)
1	Crystalline	100	0
		64.7	29.5
		45.3	54.5
		34.2	81.3
		27.5	103.5
2	Polished	100	0
		95.1	27
		92.8	51
		87.5	99.6
		56.7	161.2
3	Crystalline	44.5	228.2
		100	0
		82.7	24.1
		63.9	71.4
		50.4	133.1
4	Polished	39.1	200.0
		32.0	269.0
		28.6	330.9
		24.1	424.1
		100	0
		94.2	33.5
		88.2	89.3
		82.6	162.8
		80.0	232.3
		77.3	310.7
		74.4	383.4

The curves in Fig. 11, showing activity remaining on the anode plotted against coulometer cathode activity, were made from the data for runs 3 and 4, one employing a polished and the other a crystalline silver substrate. These curves reveal a difference in the behavior of silver electroplated on polished and crystalline substrates, since the silver electroplated on crystalline surfaces was removed much more readily than silver plated on the polished surfaces.

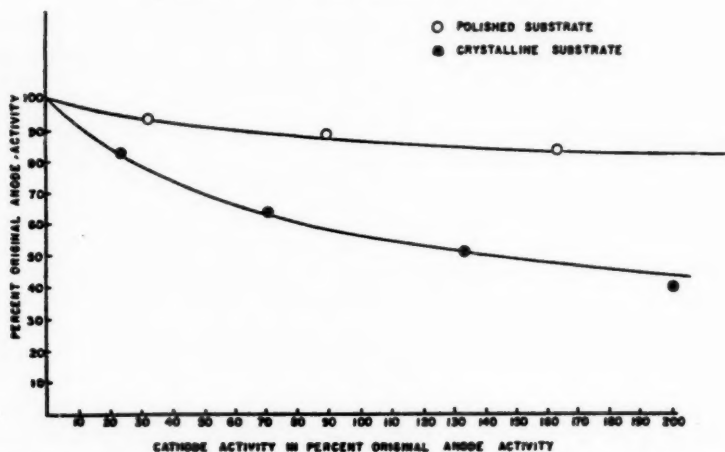


FIG. 11. Electrochemical removal of activity from polished and crystalline surfaces.

DISCUSSION

Of all the work on metal-metal ion exchanges reported to date, the experiments of the present authors seem to be the only ones where care was taken to produce either completely crystalline or completely "non-crystalline" surfaces. As was found in these experiments, etching silver foils in the "as-received" condition sometimes produces surfaces which contain a large percentage of "worked" material. The low extent of the exchanges with etched surfaces found by Baerg and Winkler indicates that the amount of "non-crystalline" material was small; this was merely fortuitous, however. In the experience of the present authors, some foils as received produced good crystalline surfaces when etched with nitric acid; however, the best crystalline surfaces, which take up the least radioactivity from a radioactive silver nitrate solution, can only be consistently produced by annealing the metal before etching.

As far as can be ascertained from the published reports, none of the other workers produced a really good polished surface either. The operation of polishing, as demonstrated years ago by Beilby (3), consists in more than a mere levelling of the surface by wearing down projections. The use of abrasives such as emery results in a cutting down of projections and a working of the surface to some extent, but crystalline metal is left exposed between the scratches made by the abrasive, as can easily be seen with a microscope. The true polishing action is performed only by using a very soft material such as chamois, kidskin, or the felt polishing cloths supplied for use on the Buehler metallographic polishers, and a very fine wet powder (alumina seems to be the best). With the microscope it can be seen that this process causes metal to flow like a liquid for a short distance. Hollows are bridged over or filled in, ridges disappear, and the whole surface becomes very smooth, lustrous, and

noncrystalline. There seems to be little doubt that the Beilby layer is "vitreous", or, in effect, a supercooled liquid. The local pressures developed must be very high, and it was shown by Bowden and Ridler (4) that the local temperature rises to the melting point of the metal. In electron diffraction studies a pattern similar to that of a liquid was obtained from a polished surface (25), and Finch, Quarrel, and Roebuck discovered that a polished surface of copper dissolved zinc atoms to form a brass, while crystalline copper under the same conditions received only a deposit of zinc metal (9). Dobinski very carefully prepared polished specimens in the absence of oxygen, and showed that the surface was amorphous (7). It is of interest that for silver he found no evidence of oxide on surfaces polished in air. Lees (20) and Hopkins (17) performed experiments which indicated that the polish layer has a depth of 30 Å. For excellent modern ideas about the "Beilby layer" Reference (23) should be consulted (papers other than Simnad's and discussions).

The rapidity of the uptake of radioactivity by crystalline surfaces and the ease of removal of 75% to 90% of it in inactive solution suggests that most of the activity acquired by such surfaces is in the form of an adsorbed layer on the surface. King and Schochet have measured the amount of silver nitrate adsorbed on silver metal powder from solutions, and the results indicate that adsorption amounts to less than one monolayer of atoms (19). A comparable value was found by Baerg and Winkler for activity which seemed to be adsorbed, and could be "plated" onto the surface by rendering the surface cathodic in the Bowden-Rideal cell. The radioactivity which was not removable by exchange with inactive solution was held by Baerg and Winkler to be incorporated into the surface layers of the crystal lattice, and the theories of this crystal growth are well discussed in their papers. Equilibration of the surface for long periods in inactive solution reduced the initial rate of exchange, probably because of the formation of electrical double layers of adsorbed inactive ions, in their view. The present authors suggest it would be expected that exchange with such layers would, if anything, be more rapid than with the crystal lattice, and that the decrease of exchange after equilibration is due to levelling of potential differences on the surfaces, as discussed below in connection with mixed surfaces.

The different behavior of highly polished surfaces indicates a different mechanism for their uptake of radioactivity. That adsorption does take place at first is shown by the deactivation experiments, where it is seen that polished surfaces which had been in the active solution for short times, down to one minute, lost up to 80% of their radioactivity when transferred to inactive solution, and that the radioactivity lost by polished surfaces was dependent on the time they had been in contact with the radioactive solution. After 17 hr. in the solution only about 30% of the acquired radioactivity was removable in this way. The rate of uptake was slower at first—this may be due partly to the smaller surface, and partly to the fact that the lack of a regular lattice makes adsorption more difficult. The regular increase of radioactivity taken up, the longer time required, and the greater retention after equilibrium is reached show that 70% of the silver ions which enter the metal become

unavailable for exchange. This can be due to changing of the surface structure as proposed by Haïssinsky, or to diffusion into the polish layer and thus away from the surface. The changing of the surface structure would presumably result from the dissolution of the anodic polish layer and the plating out of the silver ions from the solution in a crystalline form. This mechanism might explain the phenomena observed in the "controlled exchange" (Table VIII). If the silver plated out in crystalline "trees", on reversal of polarity the less noble polish material would dissolve first, leaving most of the Ag^{110} on the metal surface. Several further experiments might check this mechanism. Silver is notorious for its tendency to plate out as large "trees" from nitrate solutions, but addition agents such as gelatin make more uniform deposition possible. Plating from cyanide solution also results in smooth, uniform deposits. If this mechanism is correct, silver plated on polished substrates from silver nitrate with gelatin or from cyanide solutions should be more readily removed when the current is reversed. Similarly, the exchange between metal surface and solution should be affected if such addition agents or complexing agents are used.

The other explanation of the behavior of highly polished surfaces is that a truly "kinetic" exchange takes place between the polish layer and the solution, analogous to that between a liquid metal like mercury and an aqueous solution of one of its salts. According to this view, silver ions on the polished surface change places with silver ions which strike the surface from the solution. Because of the amorphous or vitreous state of the metal in the polish layer, the atoms or ions in it have a much greater mobility than do those in crystalline metal. Besides enhancing the exchange activity, this increased mobility allows a more rapid diffusion into the interior of the polish layer, and thus a greater extent of radioactivity uptake. The behavior of the foils which had been left for 228 days after their first activation and then did not deactivate at first with inactive solution or even lose activity when etched with dilute acid, although in radioactive solution they rapidly acquired more activity part of which was removed if the foils were again immersed in inactive solution, seems to support the diffusion hypothesis. The dissolution of zinc atoms in the polish layer on copper, reported by Finch, Quarrel, and Roebuck, and the work of Finch and Sun on electroplating onto polished substrates (10) inclines to the view that the behavior of the polished surface is due to actual entry of the ions from the solution into the liquid-like polish layer. It should be possible by further experiments, such as by pretreatment of long duration of polished surfaces in inactive solutions, and by diffusion experiments, to establish one or other of these mechanisms as the correct one.

On mixed surfaces, such as are prepared by exposing the interior of cold-worked metal, or by abrading with emery or partially polishing a crystalline surface, much of the radioactivity would seem to be acquired by electrolytic deposition onto the more crystalline portions, due to the local potential differences between the anodic worked or vitreous areas and the cathodic crystalline portions of the surface. This is shown by the autoradiographs of the surface of the cold-rolled piece, Fig. 8, and those of Simmad and Ruder. On such

a worked surface the actual area of the metal is much greater than on an annealed surface, owing to fragmentation of the crystallites, and a virtually infinite number of crystal faces with completely random orientations, of both low and high indices, is exposed. This condition greatly enhances the exchange ability of the surface, but in addition there is the electrolytic action between the anodic worked material and the cathodic ordinary crystalline material. When potential differences have been evened out, and the local currents have ceased, exchange between any vitreous material remaining and the solution can still take place, so that the final amount of radioactivity uptake and the distribution of the radioactivity depend upon the relative amounts of worked and unworked metal on the surface. Tables II and III and Fig. 7 show how the ratio of vitreous and crystalline metal affects the rate and extent of activity uptake by the surface. When the vitreous material exceeds a certain proportion the uptake of radioactivity decreases, the surface behaving more like a completely polished one.

Heat treatment of polished surfaces resulted in a revision of their behavior to that of crystalline surfaces, although these surfaces still appeared highly polished after heat treatment. It would be interesting to see whether short heat treatment results in the formation of a mixed surface before truly crystalline behavior begins.

The retention of radioactivity up to 95% by mixed surfaces when transferred to inactive solution supports the belief in the electrolytic deposition mechanism, since ions when plated onto the crystalline metal would not exchange like those merely adsorbed as in the beginning of the ordinary exchange process.

The decrease in activity uptake after long immersion in inactive solution, observed by Baerg and Winkler using abraded foils, can be explained as due to the evening out of local potential differences, so that the electrolytic action does not take place when the surface is exposed to the radioactive solution. The result of the dissolving of anodic material and the deposition onto the crystalline metal should result in the surface becoming more crystalline, or completely crystalline, if the ratio of vitreous to crystalline metal is right. With a perfectly polished surface, however, there should be no electrolytic action, and in the absence of nuclei, no recrystallization, unless nuclei are formed by the action of the solution. Rollin's observation of the effect of sodium nitrate solution on his mirror surface would indicate that the surface was activated in some way by the solution, perhaps by the formation of an absorbed double layer of sodium and nitrate ions, which exchanged rapidly with the silver nitrate solution.

The exchange with gold and platinum surfaces must be due to either adsorption, intermetallic compound formation, or a purely kinetic exchange, resulting in the formation of a solid solution, as observed by Finch *et al.* with zinc and copper. These metals are too far below silver in the electrochemical series for any electrolytic action between them. The exchange experiments with the silver amalgam, on the other hand, seem to show much electrolytic action between mercury (with a standard potential of -0.7986 v.) and vitreous and crystalline silver. (The standard potential of silver is given variously in

tables as -0.7978 v. and -0.7995 v.) Rapid kinetic exchange between mercury and silver nitrate solution probably took place also, and perhaps initiated the electrolytic action, by allowing the mercurous ions to get into the solution. It would appear that the vitreous silver displaced mercury ions from the solution, which in turn displaced silver ions onto the crystalline silver metal. The papers of Groh (12) and Kayas (18) should be consulted for the behavior of amalgams other than silver.

The exchanges with polished and mixed surfaces all follow fairly satisfactorily the empirical equation $\log x = a \log t + b$, first stated by Haïssinsky (where x is the radioactivity of the metal, t is the time of immersion, and a and b are constants which differ for each run), until a maximum value is reached, when the curve levels off. The data for the highly polished surfaces also may be expressed by the equation $\log[(x_{\infty} - x)/x_{\infty}] = kt$, where x_{∞} is the

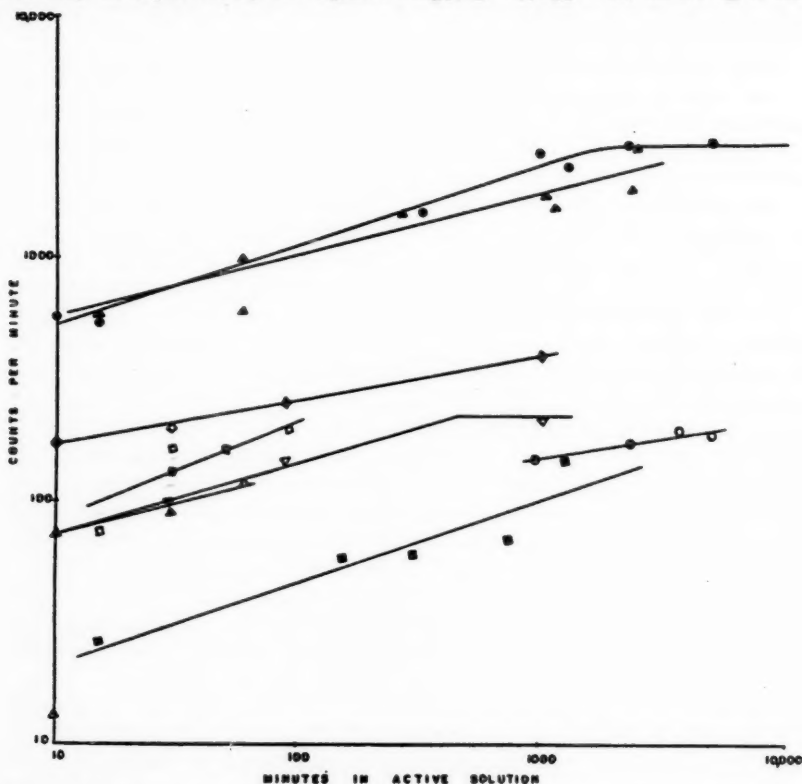


FIG. 12. The uptake of activity with time, according to the equation of Haïssinsky, $\log x = a \log t + b$.

- Data from Fig. 3
- △ Data from Fig. 5
- Data from Fig. 6
- ◇ Data from Fig. 7 (Abraded Foils)
- ▽ Data from Fig. 7 (Polished Foils)

- Data from run with solution No. 2
- Data from run with solution No. 1
- ▲ Data from run with solution No. 2

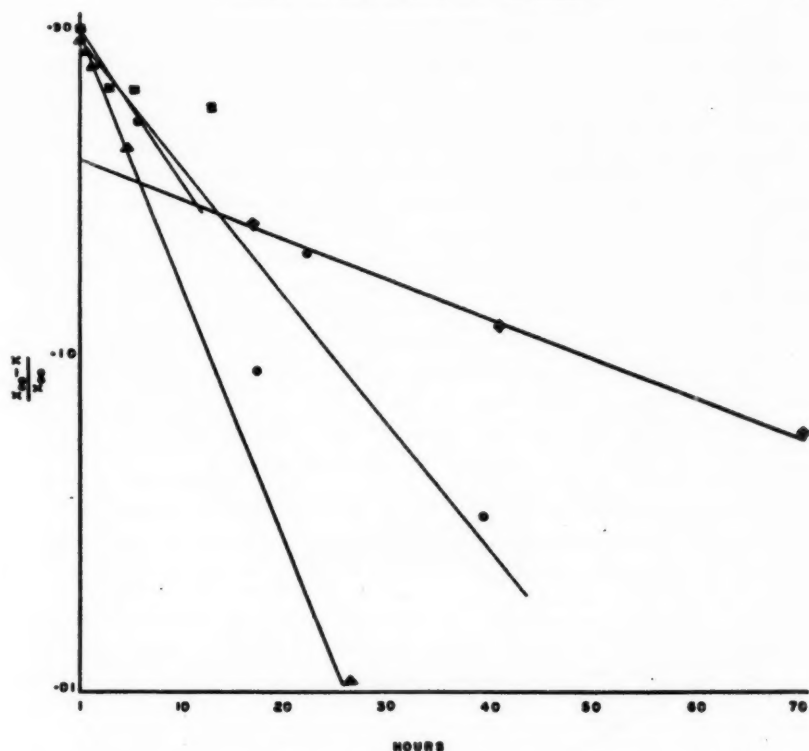


FIG. 13. The uptake of activity with time, according to the equation $\log [(x_\infty - x)/x_\infty] = kt$.

- Data from run with solution No. 2
- Data from run with solution No. 1
- ▲ Data from run with solution No. 2
- ◆ Data from Fig. 3

maximum radioactivity taken up, and x is the radioactivity at time t . This latter equation is the one followed by mercury and amalgams, as well as by silver metal powder and copper, and indicates a kinetic type of exchange. The reverse exchange (radioactive metal - inactive solution) for a mixed surface also follows the equation of Haïssinsky (with different values for the constants), but that for a highly polished surface fitted the equation $\log x = at + b$ rather better. This of course is also a first order kinetic equation, being the integrated form of the equation $dx/dt = ax$, and indicates that the concentration of radioactive atoms, x , available at the beginning of the exchange remains so during the measurements. The differential form of Haïssinsky's equation, $dx/dt = ax/t$, shows that the rate of change of activity in the metal is inversely proportional to the time, as well as being directly proportional to the initial concentration. This seems to indicate that the number of active atoms at the surface available for exchange becomes smaller in a

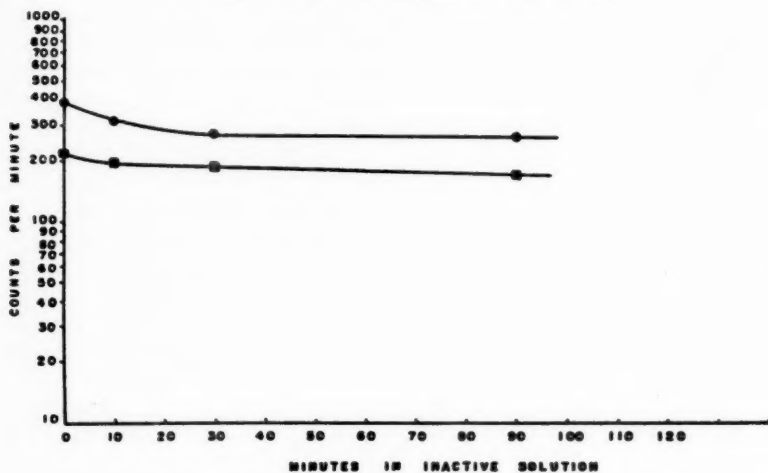


FIG. 14. The deactivation of surfaces with time.

Data from Fig. 7
 ● — Polished 60 seconds
 ■ — Polished 600 seconds

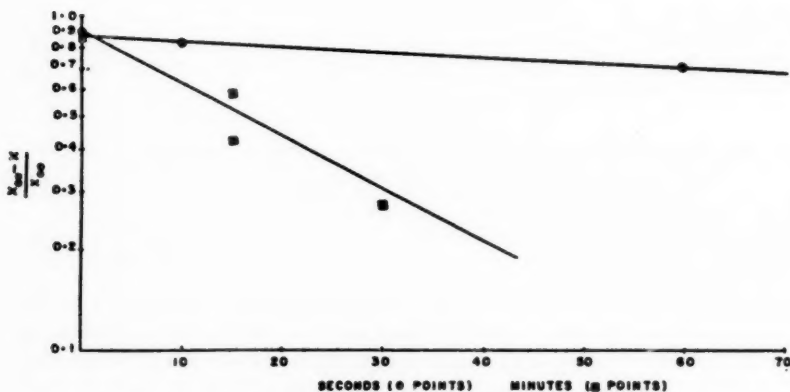


FIG. 15. The uptake of activity in short periods of exposure.

● Data from Fig. 7
 ■ Data from Fig. 6

regular manner with the passage of time. This might be due to the electrolytic action or to diffusion into the metal or to both. Pitts has derived a log-log equation to explain the exchange between silver salts and a silver solution, and concluded that a diffusion mechanism exists (21). Figs. 12, 13, 14, and 15 show how the data fit the various equations.

Gerischer and Vielstich calculated from their results the self-diffusion coefficient in silver metal. In view of the above discussion on the state of the metal, it seems to the present authors that what they measured was probably the self-diffusion coefficient in the distorted, worked metal, or along the grain boundaries, where dislocated atoms are also in a much more mobile state than in the interior of the grains (11). They would probably find a difference when they continued their work with single crystals. Winegard and Chalmers measured the self-diffusion of silver along a surface and obtained a value of 2×10^{-9} cm.²/sec. (at 400° C.) (27). They took care in the preparation of their surface (of a single crystal) to avoid forming any "flowed" metal, however.

To recapitulate, the authors, from a study of their own work and that of others who have investigated the exchanges of metals with their ions in aqueous solutions, conclude that such exchanges depend upon the state of the surface. With completely crystalline surfaces, the exchange, if it takes place at all, is of very small extent. Activity is taken up by adsorption, and perhaps by electrodeposition due to small differences of potential between different positions on the crystals. With completely polished surfaces, either the ions from the solution are plated out in a crystalline form while the anodic polish material dissolves, or else a true kinetic exchange takes place, and ions which enter the metal surface from the solution diffuse into the polish layer at a rate very much higher than that of ions in the crystals. With mixed surfaces, partly crystalline and partly amorphous, these processes both occur and in addition there is much electrolytic action between the anodic amorphous material and the cathodic crystalline material.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the assistance of W. D. Jamieson in carrying out some of the experiments, and their indebtedness to the National Research Council of Canada for two bursaries and a summer research grant, and to the Defence Research Board of Canada for a grant, number 2-1-87-156, Project D44-75-35-03.

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THE POLYMERIZATION OF ETHYLENE SENSITIZED BY ETHYL IODIDE¹

BY V. B. SEFTON² AND D. J. LE ROY

ABSTRACT

The polymerization of ethylene sensitized by the thermal decomposition of ethyl iodide in the presence of mercury vapor has been studied at 250°, 275°, and 300°C. C¹⁴-labelled ethyl iodide was used in a number of experiments. The increase in the rate of decomposition of ethyl iodide in the presence of ethylene and the formation of butyl iodide are accounted for by equilibrium processes of the type $RI + Hg = R + HgI$. The important features of the reaction were established from the identity, quantity, and activity of the various products. The predominant formation of olefins is attributed to the isomerization and decomposition of large radicals. Very little of the butane is formed by the combination of ethyl radicals. Radical disproportionation is the most important chain termination step.

The decomposition of the lower alkyl iodides has been studied extensively (10) and it is generally agreed that in both the thermal reaction and in the photolysis in the region of the continuum (*ca.* 2600 Å) the primary process consists in the formation of alkyl radicals and iodine atoms. The quantum yields of the photochemical process are low because of the back reaction but can be greatly increased by trapping the iodine atoms with mercury or silver. The thermal or photochemical decomposition of alkyl iodides in the presence of ethylene and either mercury or silver should therefore afford a convenient method for studying the free radical sensitized polymerization of ethylene.

Jungers and Yeddanapalli (5) have studied the polymerization of ethylene sensitized by the photolysis of methyl, ethyl, *n*-propyl, and isopropyl iodides in the presence of mercury at temperatures in the range 130° to 275°C. Under conditions likely to yield low radical concentrations, viz. low iodide concentrations, high ethylene concentrations, and low light intensities, they found that the "yield", defined as the ultimate pressure decrease on prolonged irradiation divided by the initial pressure of iodide, reached maximum values which were in the approximate ratio 3.5 : 3.0 : 2.5 for methyl, ethyl, and the propyl iodides, respectively. They concluded from this that the final polymer had approximately the same molecular weight in each case and that for steric reasons the growing radicals formed by the successive addition of ethylene molecules underwent chain termination when they reached a more or less common critical size. According to their mechanism all the products should be saturated, for at low radical concentrations they assumed that chain termination would take place by the reactions



while at high radical concentrations they assumed that it would occur by

¹Manuscript received September 22, 1955.

Contribution from the Department of Chemistry, University of Toronto, Toronto, Ontario.

²Present address: Canadian Industries (1954) Limited, McMasterville, Quebec.

radical combination. Radical disproportionation would also be expected to occur, in the light of more recent work (9).

Although Jungers and Yeddnapalli did not analyze their products their conclusions appeared to be well founded. However, because of the fundamental importance of polymerization reactions it seemed desirable to make a further study of the problem taking advantage of fractionation methods and infrared spectra as analytical tools. In the present work the polymerization of ethylene was initiated by the thermal decomposition of ethyl iodide in the presence of mercury. In order to obtain as much information as possible about the reactions of the ethyl radicals a number of experiments were performed using ethyl iodide labelled in the methylene group with C^{14} .

EXPERIMENTAL

The Reaction System

The reaction vessel used in most of the experiments consisted of a Pyrex cylinder having a volume of approximately two liters. The cylinder was mounted vertically and a cooling thimble was placed in the connecting tubing at the point where it emerged from the furnace. By passing compressed air through the thimble the mercury which distilled from the pool at the bottom of the cell was condensed and allowed to drop back into the cell. A mercury cutoff served to isolate the cell during an experiment and this was used as a manometer to give a rough measure of the amount of reaction taking place.

The initial ethyl iodide was measured accurately as a gas, using a separate calibrated volume and a modified Pearson gauge. It was then frozen into the cell by placing liquid air in the thimble. Ethylene was measured and admitted in the same way. The cell was filled at room temperature, and since the reaction was allowed to proceed from $4\frac{1}{2}$ to 38 hr. rapid heating was not considered essential. At the end of an experiment the temperature was lowered by cutting off the current and blowing air through the furnace. When the cell had cooled to approximately room temperature the final pressure was measured and corrected to 25°C.

For the experiments with ethylene and ethyl iodide in the absence of mercury and those with ethyl iodide and mercury in the absence of ethylene a special cell having a volume of 720 cm.³ was used. The reagents were measured as described above and condensed into the cell by immersing it in liquid air. It was then sealed off and placed in the furnace. At the end of an experiment it was sealed to the apparatus at a breakoff valve.

Reagents

The ethylene used had a rated purity of 99.5%. It was treated with 2 *N* ammoniacal silver nitrate to remove traces of acetylene, dried over Drierite and phosphorus pentoxide, and subjected to a number of trap-to-trap distillations.

The inert ethyl iodide was distilled in an 18 plate column and thoroughly degassed before being placed in a storage vessel isolated with a mercury cutoff. The active ethyl iodide, labelled with C^{14} in the methylene group, was

obtained from Tracerlab. The original 0.3 gm. sample had an activity of one millicurie. It was immediately diluted to 2 gm. with inert ethyl iodide and the portion of this used in the experiments was condensed into a storage bulb and isolated with a mercury cutoff. Both the active and inactive iodides were kept frozen with dry ice to avoid decomposition.

In preparing a sample of active ethyl iodide for an experiment suitable amounts of the active and inactive materials were removed from the storage bulbs, measured in the gas burette, and mixed. An aliquot of this material was then used to obtain the activity of the material to be used in the experiment. In a number of cases aliquots were distilled to remove any active material other than ethyl iodide which might have been present in the original sample. Since no such products could be found the distillation was subsequently eliminated.

Distillation of the Products

Ethylene and ethane were removed by distillation at -168° to -170°C . (7). Since no acetylene could be found the second fraction was taken off at an initial pressure of 1.0 mm. (ca. -100°C .), the cut being made at 0.2 mm. (ca. -50°C .). The second fraction and the residue remaining in the still were separately treated to remove iodides as described below and then redistilled into a number of fractions using initial and final takeoff pressures of the order of 0.2 and 0.05 mm., respectively. Only for the smaller fractions did the final takeoff temperature exceed the initial by as much as four or five degrees.

Separation and Analysis of the Iodides

A study of the infrared spectrum of the products showed that both ethyl and *n*-butyl iodide were present, although the initial material was free from the latter. Because of their different vapor pressures a fairly complete separation of the two was achieved in the fractionation referred to above. The iodides were removed from the fractions containing them in two ways. In the first method the fractions were frozen onto an aqueous paste of silver metanitrobenzoate which was then allowed to warm to room temperature and stand overnight, resulting in the formation of the ethyl or butyl ester and silver iodide. The residual wet gas was frozen onto solid potassium hydroxide and finally dried for 12 hr. in contact with phosphorus pentoxide. The infrared spectrum of the dried gas showed that the iodides were completely removed by this method.

To determine the amount of ethyl or butyl iodide the mixture of the ester and silver iodide was treated with warm concentrated nitric acid and then diluted with water and centrifuged. The supernatant liquid was then removed. The residual silver iodide was further extracted with 50% aqueous ethanol, filtered, dried, and weighed. Tests on known mixtures of hexane and ethyl iodide showed the method to be accurate to about 2%.

In some of the experiments with active ethyl iodide the silver metanitrobenzoate method was used in an attempt to obtain the activities of the two iodides. In this case the esters were extracted from the silver iodide with petroleum ether. After evaporating the solvent the esters were hydrolyzed

with 2 *N* sodium hydroxide; the resulting alcohols were then converted to barium carbonate as described below. However, it was found that the silver metanitrobenzoate reagent also removes quantitatively compounds with terminal unsaturation, although it does not remove other olefins to any degree. Although it was apparent that the method could not be used for the determination of the activities of the iodides it was used to remove terminally unsaturated olefins, and this made it possible to determine the activities of the remaining 2-alkenes.

The method ultimately used to determine the activities of the iodides involved their reaction with hexamethylenetetramine in chloroform solution. The resulting quaternary salt is insoluble in chloroform and was filtered off and burned for the activity determinations.

Infrared Gas Analysis

A Perkin-Elmer model 12-C instrument was used, but because of the small samples obtainable the optical arrangement was modified. The glow bar was removed from its normal position to a point on the same optical axis but about 80 cm. from the light chopper. Between the two was placed the cell, consisting of a Pyrex tube 70 cm. long and 15 mm. in diameter. The end near the glow bar was flanged out to about 40 mm. Sodium chloride windows were sealed to each end of the cell and a stopcock and cold finger were sealed to the flanged end for freezing the gas into the cell and for obtaining the blank trace. Despite the very poor optical properties of this arrangement there was an appreciable net improvement in the accuracy with which small samples of gas could be analyzed.

In setting up the quantitative analysis scheme for the hydrocarbons the spectra of a number of standard samples obtained from the United States Bureau of Standards were taken at various pressures. Because of their small extinction coefficients at usable analytical wave lengths the amount of paraffin in a sample was usually determined by subtracting the amount of olefin from the total pressure. These results were checked by taking the spectrum of the residue from the treatment of the olefin-paraffin mixture with mercuric acetate, described below.

Activity Determinations

Samples for combustion were condensed into a gas burette consisting of a number of connected bulbs, one of which contained a cold finger which could be filled with liquid air. After measuring the volume of the gas oxygen was allowed to mix with it by opening a stopcock at the top of the burette. By slowly raising the mercury in the burette the mixture was fed into a continuous stream of pure oxygen which flowed through a conventional micro-combustion tube. The carbon dioxide formed was bubbled through saturated barium hydroxide solution. The barium carbonate was collected and washed on a filter paper held in a Tracerlab E-8A precipitation apparatus. Carbon numbers calculated from the weights of dried barium carbonate were usually a few per cent low, presumably because of incomplete trapping of the carbon dioxide in the barium hydroxide solution.

The C^{14} activity of the ethyl iodide used in any particular experiment was arbitrarily given a value $A = 1$, and the activities of the various products were measured relative to this on a molar basis. To obtain A the measured number of counts per minute, C_{obs} , was first corrected for the background count C_b . A correction for self-absorption was then made using the data of Yankwick *et al.* (12). For a constant area of barium carbonate precipitate (2.83 cm.^2 , compared to our value of 2.82 cm.^2) having various weights per unit area X , they obtained a function $J(X)$ such that $(C_{obs} - C_b)/J(X)$ is equal to the number of counts per minute corrected for background and self-absorption. To allow for any variation in the sensitivity of the geiger tube the count on the sample was always followed by one, C^* , taken on a standard reference sample of barium carbonate using the same geometry. A quantity S , proportional to the specific activity of the sample, was then obtained,

$$S = \frac{(C_{obs} - C_b)/J(X)}{(C^* - C_b)W},$$

in which W is the weight of barium carbonate in the sample. The molar activity of the sample relative to that of the ethyl iodide used, referred to in the text simply as molar activity, is then given by

$$A = (S_s/S_i) N/2,$$

in which the subscripts s and i refer to the sample and to the iodide, respectively, and N is the number of carbon atoms in a molecule of product. A typical result, found for the hexane obtained in one of the experiments, is illustrated in Table I. The value of the molar activity of the hexane indicates that it contains, on the average, one ethyl radical derived from ethyl iodide.

TABLE I
DETERMINATION OF THE MOLAR ACTIVITY OF HEXANE

Material	W , mgm.	X , mgm./cm. ²	$J(X)$	$C_{obs} - C_b$, c.p.m.	$C^* - C_b$, c.p.m.	S	A
Initial ethyl iodide	20.6	7.32	0.421	12570	4370	0.331	1.00
Hexane	31.48	11.18	0.300	4350	4410	0.1045	0.95

Separation of Olefins from Paraffins

To determine the molar activity of a paraffin it was necessary to separate it from the unsaturated compounds present in the same fraction. This was accomplished by an adaptation of the hydroxy-mercurial method (8). The gas was frozen into a 100 ml. flask containing 20 ml. of saturated aqueous mercuric acetate and 10 ml. of 3% hydrogen peroxide which had previously been degassed. The flask was then warmed to room temperature and shaken, intermittently, over a period of 12 hr. The residual gas and 1 or 2 ml. of the liquid were then distilled onto solid potassium hydroxide. After several hours the contents were cooled with dry ice and the hydrocarbons distilled back into the system and measured. For compounds of higher molecular weight than bu-

tane the final drying was made with phosphorus pentoxide rather than dry ice. The infrared spectra showed complete removal of olefins by this method. Analysis of synthetic mixtures showed the method to be quantitative for mixtures of ethane and ethylene. For other olefin-paraffin mixtures there was a slight loss of paraffin; in these cases the quantity of paraffin was estimated by the infrared method.

Nonvolatile Products

After a series of experiments in which ethylene, ethyl iodide, and mercury had been used the nonvolatile material in the reaction vessel was extracted with carbon tetrachloride. The absence of an appreciable residue on evaporating the solvent indicated that no diiodoethane was present. Except for the mercury, the nonvolatile material was completely soluble in aqueous potassium iodide. Chemical tests showed the presence of mercurous iodide. The absence of diiodoethane was also confirmed in the experiments with ethyl iodide and mercury alone.

RESULTS

Products

In Table II are shown the results of pairs of experiments done at 250°, 275°, and 300°C. The amounts of the products are given in mm. pressure in the reaction vessel at 25°C. The values of $-\Delta P/-\Delta C_2H_5I$, analogous to the

TABLE II
PRODUCTS OF THE REACTION

	250°C.		275°C.		300°C.	
Experiment No.	23	27	21	22	28	25
Initial C_2H_5I	10.4	33.2	11.2	34.9	11.3	32.0
Initial C_2H_4	139.6	154.3	143.5	143.6	146.2	152.5
Time, hr.	25	24	19	17.5	7	8
$-\Delta C_2H_5I$	8.8	29.3	10.6	34.1	10.8	30.8
$-\Delta C_2H_4$	30.9	61.4	41.3	76.0	46.4	78.0
Ethane	0.64	2.04	0.5	3.6	0.9	3.6
Propane	—	0.2	—	0.37	0.38	1.5
<i>n</i> -Butane	0.89	2.9	2.2	6.3	2.3	7.0
Hexane	1.5	3.7	2.8	4.5	2.4	4.9
Total paraffin obs.	3.0	8.8	5.5	14.8	6.0	17.0
Total paraffin calc.	3.6	12.2	5.0	16.6	5.4	15.4
Propylene	0.54	0.67	1.73	2.0	3.7	5.2
Butene-1	1.87	2.1	2.5	3.2	3.1	5.2
<i>trans</i> -Butene-2	0.48	0.35	0.62	0.9	1.3	1.7
2-Methyl butene-1	1.22	0.67	1.8	1.1	1.9	1.7
Hexene-1	0.42	2.1	0.54	1.4	1.0	1.9
<i>trans</i> -Hexene-2	0.47	1.5	0.90	2.1	1.7	3.3
C_7 and higher	5.5	11.5	4.9	13.0	4.5	7.2
Total olefin obs.	10.5	18.9	13.0	23.7	17.2	26.2
Total olefin calc.	9.9	15.5	13.5	21.9	17.8	27.8
Butyl iodide	1.7	5.0	0.6	1.0	0.0	0.0
$-\Delta P$	25.5	59.5	32.9	69.3	33.5	65.6
$-\Delta P/-\Delta C_2H_5I$	2.9	2.4	3.1	2.0	3.1	2.1
Olefin/paraffin obs.	3.5	2.1	2.4	1.6	2.9	1.5
Olefin/paraffin calc.	2.7	1.3	2.7	1.3	3.3	1.8

"yield" of Jungers and Yeddanapalli (5), are seen to be sensitive to the initial iodide pressure but relatively insensitive to temperature, in agreement with their observations. The value of approximately three for low iodide pressures is identical with their value for low ethyl radical concentrations. However, instead of the products being all saturated, as they predicted, it is seen that there is considerably more olefin than paraffin. The proportion of olefin is greater for low than for high ethyl iodide concentrations, and even in the latter case the amount is greater than could be accounted for by disproportionation.

Qualitative infrared analysis of the fraction listed in Table II as "C₇ and higher" showed it to be composed of hydrocarbons containing the groups $\text{CH}_2=\text{C}-\text{R}$ and $\text{CH}_2=\text{CHR}$, in which R and R' are saturated radicals. The



amount of this fraction was determined as the difference between the total final pressure and the sum of remaining individual product pressures. From the carbon balance of the reagents and products the average carbon number of this fraction was found to be approximately nine.

After treating the C₈ fraction with mercuric acetate it was possible to identify a hydrocarbon having an important band at 10.10 microns. Because of the small amount present it could not be positively identified, although the spectrum strongly resembled that of methyl cyclopentane. It was estimated that it could have amounted to 10 to 20% of the C₈ "paraffin".

Since the only products formed were alkanes, mono-olefins, cycloparaffins, and butyl iodide, it follows that the amount of paraffin produced must be equal to one half of the difference between the amount of ethyl iodide consumed and the amount of butyl iodide formed. The values of "Total paraffin calc." listed in Table II were obtained in this way; "Total olefin calc." was obtained by difference.

No evidence could be found for either methane or hydrogen. Pentane, if formed, did not exceed 5% of the sum of butane and hexane. The maximum amounts of pentene-1, cyclopentane, or cyclohexane that could be present were estimated to be less than 0.1 mm. The amount of *cis*-butene-2 could not exceed 20% of the *trans* isomer. The maximum amount of hydrogen iodide was estimated to be less than 0.01 mm.

Isotope Effect in the Decomposition of Ethyl Iodide

An appreciable carbon isotope effect has been observed in the thermal decomposition of a number of organic compounds (4) in which the decomposition has involved the rupture of C—C bonds. In the present instance a rupture of a C—I bond is involved. In most of the experiments a large part of the ethyl iodide was decomposed and hence, even if there were an isotope effect, the proportion of C¹⁴ in the ethyl radicals formed would be approximately the same as in the original ethyl iodide. However, the proportion of inactive ethyl radicals might be greater at the beginning of an experiment when the ethyl radical concentration is higher and the instantaneous value of the

"yield" is lower. Erroneous conclusions might therefore be drawn from the final measured activities of the products. To ascertain if the isotope effect were significant experiments were performed in which considerably different amounts of active ethyl iodide were decomposed in the presence of mercury but in the absence of ethylene. The results are shown in Table III. The acti-

TABLE III
DECOMPOSITION OF C^{14} -LABELLED ETHYL IODIDE
IN THE PRESENCE OF MERCURY

Experiment No.	31	32
Temperature, °C.	250	300
Initial ethyl iodide, mm.	38.6	39.2
Final ethyl iodide, mm.	36.2	24.0
Time, hr.	11	4.5
Ethylene formed, mm.	0.8	1.8
Ethane formed, mm.	1.2	7.1
Butene formed, mm.	—	0.4
Butane formed, mm.	—	1.6
<i>S</i> for initial iodide:		
1st sample	0.398	0.418
2nd sample	0.385	0.389
<i>S</i> for final iodide	0.384	0.404
<i>S</i> for C_2 fraction	0.378	0.410
<i>S</i> for C_4 fraction	—	0.395

vities are given in terms of the quantity *S*, defined previously. It is clear from the table that the variations in *S* are within the probable error of its determination and that the decomposition of ethyl iodide does not involve an appreciable isotope effect.

TABLE IV
MOLAR ACTIVITIES OF THE PRODUCTS

	250°C.								275°C.	
	11	13	14	12	17	27	15		21	29
Experiment No.	30.4	77.9	4.0	10.7	24.5	33.2	34.0		11.2	34.2
Initial ethyl iodide, mm.	69.4	69.5	141.2	137.8	136.8	154.3	134.5		143.5	151.3
Initial ethylene, mm.	15	16	16.5	16	38	24	17		19	6.8
Time, hr.	1.2	4.7	—	0.4	1.9	2.0	1.8		0.5	2.5
Ethane formed, mm.	0.4	1.0	—	1.1	0.8	0.5	0.4		0.9	—
Ethylene formed, mm.*	5	8	—	—	9	12	10		5	15
Total alkanes formed, mm.	21.4	61.5	2.3	5.3	—	5.0	—		0.6	—
Butyl iodide formed, mm.										
Ethane	1.0	1.0	—	0.89	0.83	1.0	0.89		0.83	1.05
Propylene	—	—	—	—	0.30	—	—		0.36	0.36
Butane	0.92	1.1	0.56	0.8	0.94	0.92	0.88		0.74	1.04
Butene-1	0.4	—	—	—	0.1	0.4	0.3		0.5	0.4
<i>trans</i> Butene-2}†	—	—	—	—	—	0.4	—		0.5	—
2-Methyl butene-1	0.99	0.94	0.72	0.72	0.87	0.96	0.96		0.69	—
Hexane	—	—	—	—	0.87	0.9	0.84		0.69	—
Hexene-1	—	—	—	—	—	—	—		—	—
<i>trans</i> Hexene-2}†	1.7	1.7	—	1.04	1.2	—	1.08		1.1	—
C_7 and higher†	—	—	—	—	—	0.7	—		—	0.6
Butyl iodide	—	—	—	—	—	—	—		—	—

* Amount present with molar activity of unity.

† Calculated from composition of fraction and activities before and after removing olefin.

‡ Based on an average carbon number of nine.

Activity of the Products

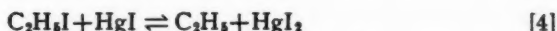
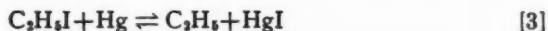
The results of a series of experiments using active ethyl iodide are shown in Table IV.

The use of a tracer does not make it possible to determine the amount of ethylene formed in the reaction since it might not have originated from ethyl iodide. However, the minimum amount formed can be estimated on the assumption that it would have a molar activity of unity. The values given in Table IV for ethylene formed were obtained in this way. About all that can be said with certainty is that some ethylene is formed and that its amount is probably of the same order as that of the ethane.

Experiments 11 and 13 are of particular interest because of the very large amounts of *n*-butyl iodide formed when the concentration of ethyl iodide approaches that of the ethylene.

DISCUSSION

One would infer from previous work that the initial process involves the decomposition of ethyl iodide into an ethyl radical and an iodine atom. However, a comparison of the results of experiment 31 (Table III) and experiment 27 (Table II) shows that the presence of ethylene greatly accelerates the rate of decomposition of ethyl iodide, which suggests that equilibria of the following type may be involved.



The addition of ethylene would lower the ethyl radical concentration and accelerate the decomposition of ethyl iodide.

Although the initial stages of the polymerization of ethylene undoubtedly consist in the successive addition of ethylene to ethyl radicals, a number of possible steps can be suggested for the formation of the ultimate products from the linear 1-alkyl radicals produced in this way.

(i) Reaction with Ethyl Iodide to Form a Linear Alkane (Reaction [1])

It has been suggested by a number of workers that reactions of this type play an important role in the photolysis of ethyl iodide (5, 11). However, their evidence is by no means convincing. West and Schlessinger (11) found that methylene iodide was formed in the photolysis of methyl iodide provided no "getter" was used to trap the iodine; in the presence of silver none was formed. In the case of ethyl iodide they found no ethylene iodide under either circumstance. Jungers and Yeddenapalli (5) did not subject their products to chemical analysis, but simply quoted the results of West *et al.* as showing that [1] would occur at high concentrations of ethyl iodide. We were unable to find ethylene iodide under any conditions.

If it were formed, the radical $\text{C}_2\text{H}_4\text{I}$ could conceivably disappear in a number of ways. If it decomposed to form ethylene and an iodine atom, or if it reacted with mercury to form ethylene and mercurous iodide, then 1 mole of active

ethylene would have to be formed for every mole of alkane formed by [1] or every mole of ethyl iodide decomposed by [1]. However, it is evident from Table IV that the amount of ethylene formed with a molar activity of unity did not exceed one-eighth of the total alkanes even at high concentrations of ethyl iodide. The possibility that the C_2H_4I radical could react with ethyl iodide to form ethylene iodide can be eliminated since the latter was not formed. If it reacted with alkyl radicals to form higher alkyl iodides, then these, in particular butyl iodide, would be expected to have a molar activity of two, which was not the case. Furthermore, in experiments 11 and 13 (Table IV) the amount of butyl iodide formed far exceeded the amount of alkanes produced, which could not be the case if reaction [1] had occurred. A suggested mechanism for the formation of butyl iodide will be given later.

(ii) *Combination of Radicals to Form Linear Alkanes*

It is evident from the olefin/paraffin ratios given in Table II that this process does not play a leading role. It can also be shown that only a small proportion of the paraffin could be formed in this way. The molar activity of the butane is much less than two. If it were formed by the combination of ethyl radicals a considerable proportion of the latter would have to be inert, i.e. arise from processes other than the decomposition of ethyl iodide. Since it is reasonable to assume that ethane is formed from ethyl radicals, it would follow that the molar activity of the ethane would have to be of the order of 0.5 or less, in disagreement with the data of Table IV. The same argument applies to the formation of hexane and higher paraffins.

(iii) *Disproportionation of Radicals to Form Alkanes and Either Cycloparaffins or Olefins*

This process would lead to olefin/paraffin ratios of unity or, if any combination took place as well, less than unity. While disproportionation cannot account for the major part of the olefin (and cycloparaffin) it can account for the alkanes and the corresponding amount of olefin.

(iv) *Hydrogen Abstraction from Olefins*

Reactions of this type can be discounted since the radicals of the vinyl type formed in this way would be certain to yield, ultimately, some diolefin, and no evidence for this could be obtained.

(v) *Decomposition of Radicals to Yield Olefins or Cycloparaffins, and an Alkyl Radical*

Reactions of this type must account not only for the compounds having an odd number of carbon atoms but also for the major portion of the olefin produced. It is readily seen, however, that a simple C—C bond rupture followed by the isomerization of the biradical is not the most probable process, as only inert olefins would be formed in this way.

If the observed olefin activities were due to disproportionation reactions, which involve two radicals, then the ratio of active to inactive butene would be expected to increase markedly with the radical, i.e. the ethyl iodide, concentration. Evidence for this is not conclusive. The results of experiments 17, 27, and 15 given in Table IV indicate an increase in the activity of the butene when

the ethyl iodide pressure is increased, but similar experiments at 275°C. show a decrease in the molar activity of the butene from 0.5 to 0.4 when the ethyl iodide pressure is increased from 11.2 to 34.2 mm.

In their experiments on tetramethylene biradicals Bawn and Milsted reported "butylene" as one of their products but did not identify the particular isomer (2). Benson and Kistiakowsky (3), on the other hand, found cyclobutane to be the only C_4 product from the photolysis of cyclopentanone and questioned the previous conclusions of Norrish *et al.* (1). It seems likely, therefore, that if tetramethylene biradicals were formed by the decomposition of a linear alkyl radical some evidence of cyclobutane would be found. This was not the case.

Kossiakoff and Rice (6) have pointed out that in many cases the activation energy for the isomerization of a long-chain free radical is much less than the activation energy for its decomposition and that as a result there should be an equilibrium process involving isomeric forms of the free radical. In particular, they suggest that 1-hexyl radicals should isomerize readily by a 1-5 shift of the free valence to form 2-hexyl radicals. Furthermore, the latter should decompose more readily than the 1-hexyl isomer since propylene and a propyl radical would be formed in a single step. The propylene formed in this way would be active.

It is evident that 1-hexyl-5- C^{14} radicals can give rise to 2-hexyl-2- C^{14} radicals by a 1-5 shift of the free valence, or to 1-hexyl-2- C^{14} radicals by a 1-6 shift. The latter could isomerize to 2-hexyl-5- C^{14} by a 1-5 shift. Similar considerations may be applied to other large radicals. Their disproportionation will yield paraffins and olefins with molar activities of unity; their decomposition will yield olefins with molar activities less than unity.

Isomerization of 1-alkyl radicals is undoubtedly involved in the formation of olefins containing the group $CH_2=C-R$. If the 2-methyl butene-1 were pro-



duced by the addition of (active) ethyl radicals to propylene, followed by the disproportionation of the resulting 2-methyl butyl-1 radical with another radical, then its molar activity would be at least as great as unity. The observed activity of less than 0.5 suggests that it arises through the addition of ethylene to 2-hexyl-2- C^{14} or 2-hexyl-5- C^{14} radicals, followed by a 1-7 and then a 1-5 shift of the free valence. Subsequent decomposition of the radical could yield either 2-methyl butene-1 and a propyl radical, or 2-methyl hexene-1 and a methyl radical. The molar activity of the pentene would be less than that of the heptene. As mentioned previously, evidence for compounds of the latter type was found in the " C_7 and higher" fraction.

The postulate that radical decomposition is usually preceded by isomerization of the original 1-alkyl radicals also affords an explanation for the fact that the activities of the ethane and butane are slightly less than unity. The decomposition of large radicals into olefins will give rise to some radicals having molar activities less than unity. The ethane and butane formed by the disproportionation of ethyl or butyl radicals with larger radicals will then have activities somewhat less than unity. This is supported by the fact that in any

particular experiment the molar activities of the ethane and butane were closely related, as shown in Table V. It is also seen that the activities of these

TABLE V
COMPARISON OF MOLAR ACTIVITIES OF ETHANE AND BUTANE

Expt. No.	Temp., °C.	Molar activity of ethane	Molar activity of butane	Olefin/paraffin calc.
27	250	1.0	0.92	1.3
21	275	0.83	0.74	2.7
28	300	0.71	0.68	3.3

products are lower in the experiments in which the olefin/paraffin ratio was high, i.e. in the experiments in which radical decomposition was more important.

(vi) *Formation of Butyl Iodide*

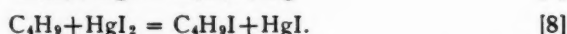
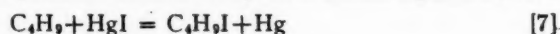
It is significant that no butyl iodide was formed in the absence of ethylene. Also, its molar activity is less than unity, whereas it would be greater than unity if it were formed by the reaction



In experiments performed at 250°, 275°, and 300°C. with ethyl iodide and ethylene but in the absence of mercury there was no butyl iodide formed, which shows that its method of production is not through the reaction



Evidence has already been given to show that the decomposition of ethyl iodide in the presence of mercury and the mercury iodides involves equilibrium processes. If so, butyl radicals could take part in similar equilibria, viz.,



Reactions of this type appear to afford the most satisfactory explanation for the formation of butyl iodide. The fact that its molar activity is somewhat less than that of the butane suggests that a small amount of the latter is probably formed by the combination of ethyl radicals.

SUMMARY

The use of C¹⁴-labelled ethyl iodide together with extensive chemical analysis of the products has revealed a number of features of the ethyl iodide sensitized polymerization of ethylene not previously established. Some of these features apply specifically to the use of alkyl iodides as sources of free radicals while others would be expected to apply quite generally to the free radical sensitized polymerization of olefins.

The primary process in the presence of mercury has long been considered to be a C—I bond rupture, followed by the reaction of the iodine atom with mercury,



However, the fact that butyl iodide was only formed in the presence of mercury (and ethylene), and the fact that ethylene accelerates the rate of decomposition of ethyl iodide suggest that [11] is the primary process in the decomposition of alkyl iodides.



It is evident that if [10], as well as [9], is considered to be a reversible process then in the absence of reactions other than those indicated it is immaterial whether [9] or [11] is considered to be the primary process, since $K_{11} = K_9 \cdot K_{10}$.

The present experiments confirm previous evidence that larger 1-alkyl radicals are built up by the successive addition of ethylene to ethyl radicals,



etc.

The concentrations of the radicals would be expected to decrease in the order ethyl, butyl, hexyl, etc., since radical growth can be terminated at any stage. This is in keeping with the fact that butyl iodide was formed (by the reverse of [11]), but not hexyl or higher iodides.

The large olefin/paraffin ratios and the formation of products containing an odd number of carbon atoms show that the decomposition of large radicals into olefins and smaller alkyl radicals plays a major role under the experimental conditions used. Furthermore, the structures and molar activities of these olefins indicate that in many cases the large 1-alkyl radicals isomerize by 1-5 and 1-6 (and presumably other) shifts of the free valence before they decompose. As would be expected, the radical decomposition reactions are more important at low than at high radical concentrations.

Chain termination occurs by both combination and disproportionation of radicals, but the latter appeared to be the more important.

ACKNOWLEDGMENT

The authors are grateful to the National Research Council of Canada for the financial assistance they have given to this research and for the Fellowship awarded to one of them (V. B. S.).

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THE EFFECT OF ATMOSPHERE DEPLETION IN SPHERICAL DIFFUSION FLAMES¹

BY R. J. CVETANOVIC

ABSTRACT

Solutions of the second order non-linear differential equation of spherical diffusion flames have been obtained for the range of conditions of experimental interest. Deviations from the simplified exponential solution are presented in a form suitable for their direct evaluation. Some recent contributions to the theory of the method are discussed.

INTRODUCTION

The diffusion flame method of Hartel and Polanyi (5) is used for determination of the rate constants of some fast gas reactions. It is based on a comparison of the rate of reaction with the rate of diffusion of one of the two reactants. The latter is introduced through a nozzle into the reaction zone where it spreads by diffusion and encounters the other reacting substance, the "atmosphere reactant". The original theoretical treatment of the method implied the following three simplifying assumptions:

1. The mass flow of the two reactants can be neglected.
2. There is a spherical symmetry in the distribution of the nozzle reactant in the reaction zone.
3. The concentration of the atmosphere reactant is constant throughout the reaction zone.

In the steady state the general diffusion equation reduces then to the form

$$[1] \quad \frac{d^2 y}{dr^2} + \frac{2}{r} \frac{dy}{dr} - \frac{k_p}{D_p} yz = 0$$

where y and z are the concentrations of the nozzle and the atmosphere reactant, respectively, D_p is the diffusion coefficient of the former in the gas mixture, k_p is the value of the rate constant to this approximation, and r is the radius of the spherical reaction zone. Since z is assumed constant and equal to z_∞ , the concentration outside the reaction zone, and y vanishes as $r \rightarrow \infty$, the solution of [1] is

$$[2] \quad y = (A_p/r) \exp(-rC_p), \quad \text{where } C_p = (k_p z_\infty / D_p)^{1/2}.$$

From the values of y , y_1 , and y_2 at two points, r_1 and r_2 ($r_2 > r_1$), the rate constant can be calculated using the expression

$$[3] \quad C_p = \ln(y_1 r_1 / y_2 r_2) / (r_2 - r_1).$$

Since its introduction in 1930 the diffusion flame method has been widely used and a large number of experimental determinations have been reported

¹Manuscript received September 15, 1955.

Contribution from the Division of Applied Chemistry, National Research Council, Ottawa, Canada. Issued as N.R.C. No. 3812.

in the literature. The method was originally devised and is particularly suited for determination of the rates of reaction of sodium atoms, which are introduced into the reaction zone through the nozzle in a stream of an inert carrier gas. The extent of penetration of sodium in the reaction zone for given steady state conditions is established by optical means. An important extension of the method has recently been proposed by Kistiakowsky and his co-workers (2, 3), who based the evaluation of the rate constant on an exploration of the temperature pattern of the spherical reaction zone. The particular significance of the temperature pattern method lies in its potential applicability to a wider variety of processes, possibly also to some atomic and free radical reactions which may be difficult to evaluate quantitatively by other means.

At present, it appears impossible to treat mathematically the general case of a diffusion flame and take into account all the details of the process. The quantitative usefulness of the spherical diffusion method depends, therefore, on how closely the simplified model suggested by Hartel and Polanyi can be approached experimentally. After the early realizations of a large uncertainty in this respect, a thorough empirical study by Heller (6) resulted in a specification of the ranges of experimental conditions within which the simple model was considered valid to a good approximation. An attempt to extend the use of the method to very fast reactions (4) resulted in the observation of the formation of "core" flames, the flames assumed to contain a core of unreacted sodium into which no atmosphere reactant did penetrate. The calculated rate constants were strongly pressure dependent and a drastic change in experimental conditions was necessitated.

In a previous paper (1) a more elaborate model was considered and the theoretical treatment extended to take into account the fact that the atmosphere reactant is consumed in the reaction and its concentration is not constant in the reaction zone. It was shown that when the mass flow of the reactants is neglected, the spherical diffusion process is described by the differential equation

$$[4] \quad \frac{d^2 y}{dr^2} + \frac{2}{r} \frac{dy}{dr} - \frac{k}{D_s} y^2 + \frac{k y_1 r_1}{D_s} \frac{y}{r} + \frac{k(z_\infty - z_1) r_1}{D_s} \frac{y}{r} - \frac{k z_\infty}{D_s} y = 0,$$

where D_s is the diffusion coefficient of the atmosphere reactant and z_1 its concentration at some particular value of the radius (r_1), and of which Equation [1] is a special case. Analysis of the derived expressions and of the single numerical solution available at the time for a particular set of experimental results showed that for relatively slower reactions the effect of the depletion of the atmosphere reactant by virtue of its consumption in the reaction was not large and that more appreciable effects could be expected for very fast reactions. Any quantitative conclusions in this respect, however, required solutions of Equation [4] for a wide variety of experimental conditions.

A function representing the generalized solution of Equation [4] has now been tabulated for selected cases covering the range of experimental interest. In the present article summarized results of the performed computations are given and their implications discussed.

Solutions of the Non-linear Differential Equation of the Spherical Diffusion Process

The radius r_1 and the corresponding concentrations of the two reactants, y_1 and z_1 , in Equation [4] are in no way specified. It is, therefore, permissible to take for r_1 the particular value of r at which $z_1 = 0$, without having to consider, for the moment, how the values of y_1 and r_1 can be ascertained. Defining r_1 in this manner and writing

$$[5] \quad v = \frac{r}{r_1} \frac{yD_2}{y_1D_2 + z_\infty D_2}, \quad x = \frac{r}{r_1} \frac{z_\infty D_2}{y_1D_2 + z_\infty D_2}, \quad K = \frac{kx_\infty}{D_2} \left(\frac{r_1}{x_1} \right)^2 = C^2 \left(\frac{r_1}{x_1} \right)^2$$

and consequently

$$[6] \quad x(r_1) = x_1 = 1/(1 + y_1 D_2 / z_\infty D_2), \quad 0 < x_1 < 1, \quad v(x_1) = v_1 = 1 - x_1,$$

the differential Equation [4] is transformed into the following generalized non-dimensional form

$$[7] \quad \frac{d^2 v}{dx^2} = \frac{Kv}{x}(v + x - 1).$$

In view of the relations [6] and subject to the condition that $v \rightarrow 0$ when $x \rightarrow \infty$, the solution of [7] is

$$[8] \quad v = \phi(K, x_1, x).$$

The function v has been tabulated for the following values of K and x_1 :

x_1	Values of K									
.99	.001	.005	.01	.05	.1	.5	1	5		
.8	.001	.005	.01	.05	.1	.5	1	5		
.6		.005	.01	.05	.1	.5	1	5	10	
.4			.01	.05	.1	.5	1	5	10	
.2				.05	.1	.5	1	5	10	50
.1					.1	.5	1	5	10	50

The solutions have been obtained numerically by the Computation Centre of the University of Toronto and the details of the computational technique employed are given elsewhere (9). The tables of the computed values will be supplied on request. They lend themselves to graphical interpolation and can be readily used for the calculation of the rate constants for any of the usual experimental conditions. For most experimental applications, however, the graphs and the tables in the following section will give directly the magnitude of the deviation from the rate constants obtained from the simplified exponential solution given in Equations [2] and [3].

Deviations from the Exponential Solutions

(a) *The Diffusion Flame Method (The "Two-point Boundary" Method)*

The rate constants, k_p , obtained from the exponential solution can be calculated from Equation [3]. Taking into account relationships [5] and [6] it is readily seen that

$$[9] \quad \delta = \frac{k}{k_p} = K(x_2 - x_1)^2 / \left(\ln \frac{v_1}{v_2} \right)^2.$$

The correction factor δ is a function of K , x_1 , and x_2 or, equally well, of K , x_1 , and v_2 . It was found convenient to calculate and plot the values of δ for

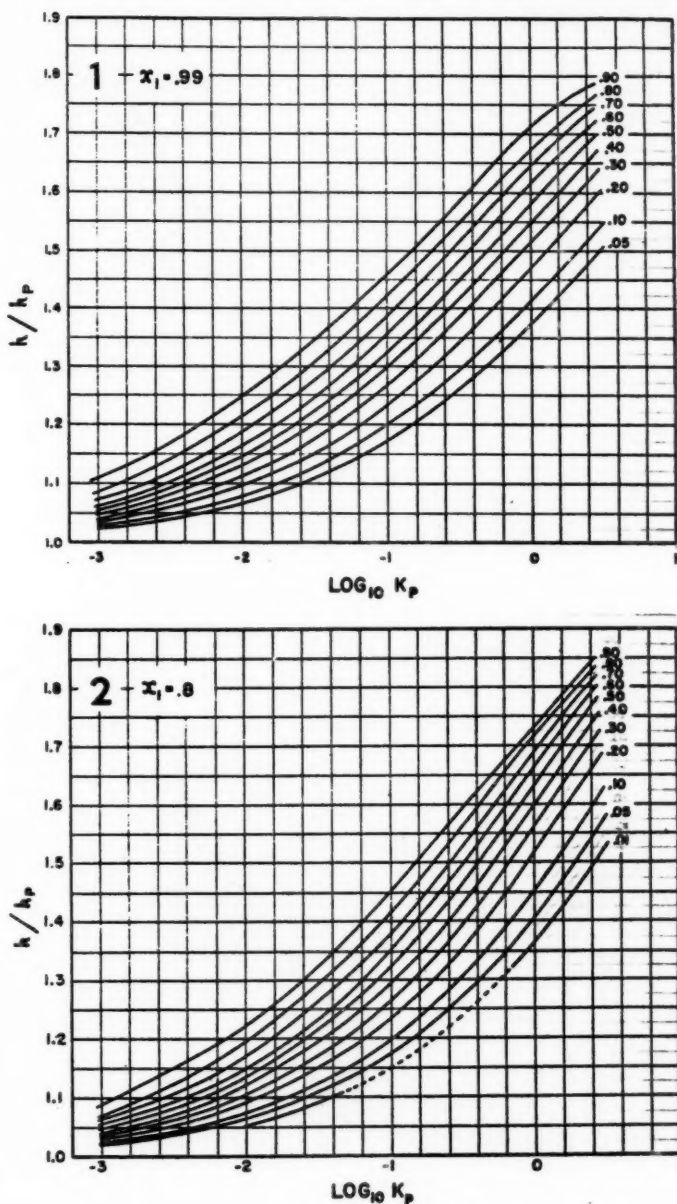


FIG. 1. Deviation factors for $x_1 = 0.99$. The numbers on the curves are v_2/v_1 ratios.

FIG. 2. Deviation factors for $x_1 = 0.8$. The numbers on the curves are v_2/v_1 ratios.

various K and x_1 values at different v_2/v_1 ratios. For $x_1 = 0.99, 0.8, 0.6$, and 0.4 the correction factors are given in Figs. 1-4; the numbers on the curves

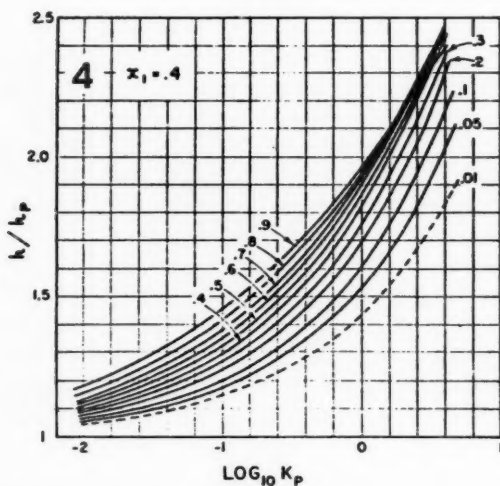
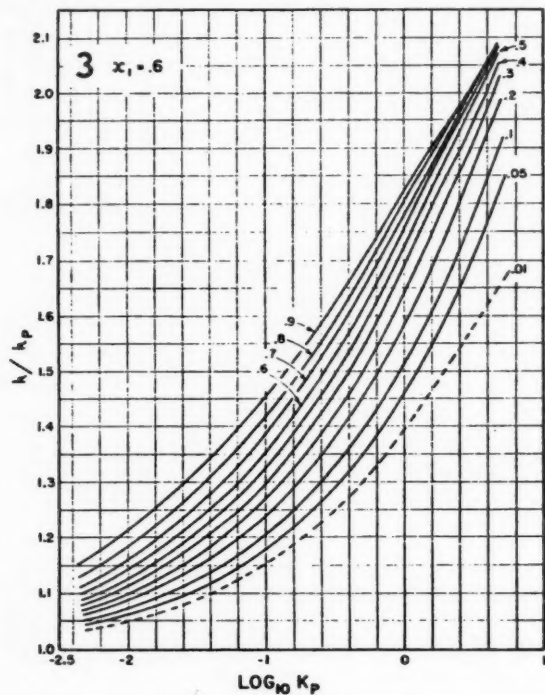


FIG. 3. Deviation factors for $x_1 = 0.6$. The numbers on the curves are v_2/v_1 ratios.

FIG. 4. Deviation factors for $x_1 = 0.4$. The numbers on the curves are v_2/v_1 ratios.

are the v_2/v_1 ratios. For $x_1 = 0.2$ and 0.1 the correction factors are given (as a function of K and v_2/v_1) in Table I, since small scale plots were not feasible

TABLE I
DEVIATION FACTORS ($\delta = k/k_p$) FOR $x_1 = 0.2$ AND 0.1 , FOR DIFFERENT K AND v_2/v_1 RATIOS

v_2/v_1	K							
	0.05	0.1	0.5	1	5	10	50	100
$x_1 = 0.2$								
.90	1.28	1.38	1.72	1.96	2.76	3.29	5.21	6.33
.80	1.25	1.35	1.69	1.93	2.80	3.41	5.89	7.61
.70	1.23	1.32	1.66	1.89	2.81	3.49	6.57	9.10
.60	1.22	1.30	1.62	1.85	2.79	3.51	7.13	10.55
.50	1.20	1.28	1.59	1.81	2.75	3.49	7.48	11.62
.40	1.19	1.26	1.55	1.77	2.68	3.42	7.56	12.05
.30	1.17	1.24	1.51	1.72	2.58	3.30	7.35	11.78
.20	1.15	1.22	1.47	1.65	2.46	3.12	6.85	10.84
.10	1.13	1.19	1.41	1.57	2.27	2.85	5.97	9.19
.05	1.12	1.17	1.36	1.51	2.12	2.63	5.27	7.88
$x_1 = 0.1$								
.90		1.35	1.79	2.11	3.50	4.65	9.98	14.54
.80		1.32	1.74	2.06	3.53	4.86	12.78	20.82
.70		1.30	1.70	2.02	3.51	4.92	14.42	25.73
.60		1.28	1.66	1.97	3.44	4.86	14.98	27.62
.50		1.27	1.63	1.91	3.33	4.71	14.62	27.07
.40		1.25	1.59	1.86	3.19	4.49	13.66	24.99
.30		1.23	1.54	1.79	3.02	4.20	12.30	22.01
.20		1.21	1.49	1.72	2.81	3.85	10.61	18.42
.10		1.18	1.43	1.62	2.54	3.37	8.53	14.18
.05		1.16	1.38	1.55	2.34	3.03	6.81	—

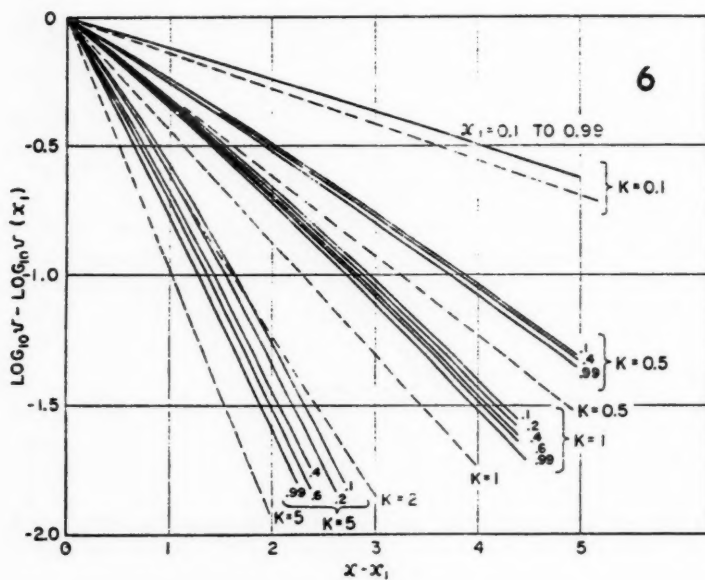
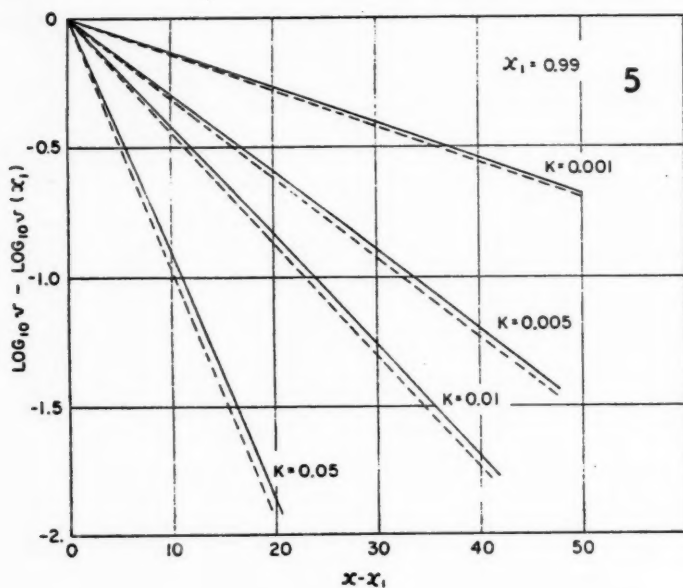
because of overlapping of some of the curves. In Figs. 1 to 4 δ is plotted against K_p , where

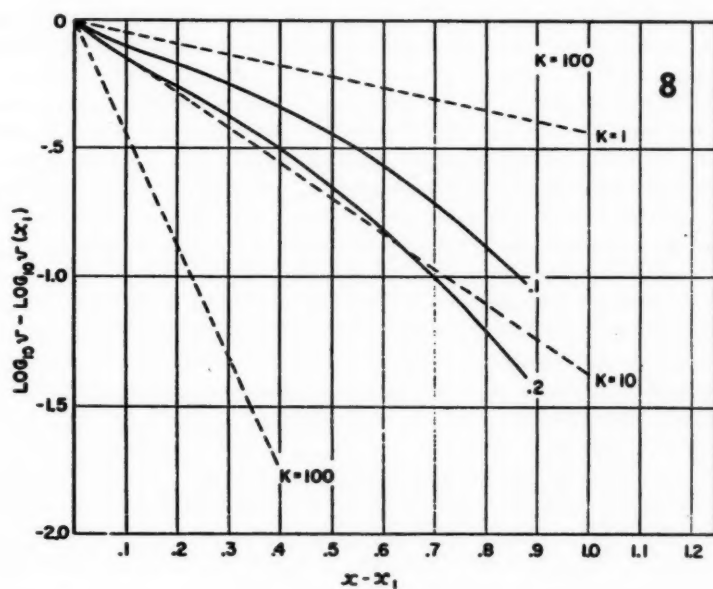
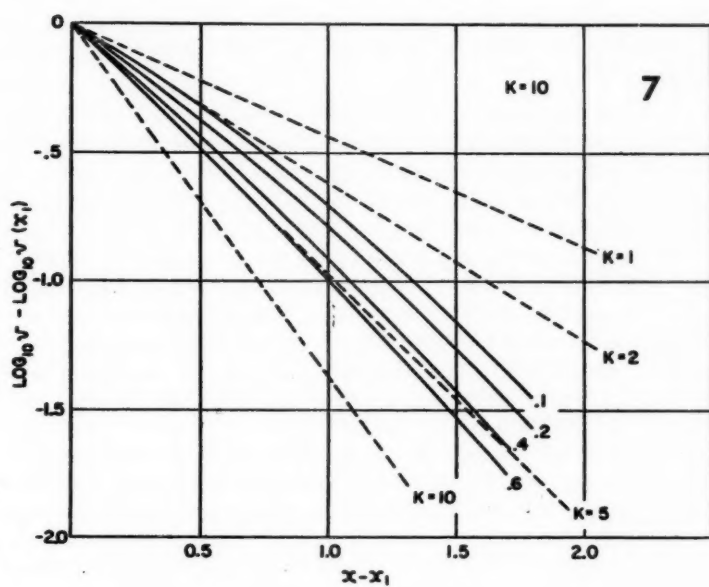
$$[10] \quad K_p = K/\delta = C_p^2(r_1/x_1)^2,$$

and not against K , because K_p can be readily calculated for given experimental conditions as well as x_1 and v_2/v_1 , and the use of the graphs is thus made quite simple. The values of the rate constants are obtained from the relationship $k = k_p \times \delta$, after calculating k_p from Equation [3] and establishing δ by the use of the graphs.

(b) The Concentration Pattern Method

In the application of the "temperature pattern" method of Garvin and Kistiakowsky (3) a quantity proportional to the product of the concentration of the nozzle reactant and τ at different values of τ is obtained experimentally. Inasmuch as the exponential solution [2] is valid, a plot of \log_e of this quantity against τ should yield a straight line the slope of which is equal to $(-C_p)$. Equally well, a plot of $\log_e v$ against x would result in a straight line with a slope of $(-C_p r_1/x_1)$. The latter plots for some of the computed cases are given in Figs. 5-8, in which $\log_{10}(v/v_1)$ is plotted against $(x-x_1)$, as shown by full lines, for the values of x_1 indicated by the numbers on the lines and several values of K . The broken lines show the corresponding plots which would be

FIG. 5. $\text{Log}(v/v_1)$ plots.FIG. 6. $\text{Log}(v/v_1)$ plots.

FIG. 7. $\log(v/v_1)$ plots.FIG. 8. $\log(v/v_1)$ plots.

obtained for different values of K provided the exponential solutions were valid. The deviations can be estimated by comparing the slopes, since the ratio of the slopes is equal to the square root of the ratio of the corresponding rate constants.

DISCUSSION

Deviations in the Hartel-Polanyi Method (The Two-point Boundary Method)

From their definition it is evident that the quantities K and x_1 under the usual experimental conditions will vary as the value of the rate constant varies. With increasing speed of the reaction K will in general increase and x_1 decrease. It is clear from Figs. 1-4 and Table I that the deviation factor differs appreciably from unity even for quite slow reactions and becomes large for very fast reactions. Furthermore, for larger v_2/v_1 ratios, which correspond to smaller "flames", the deviation is greater. These results confirm the previous intuitive qualitative conclusions. In addition, since K becomes smaller for smaller r_1 , the deviation is also decreased, showing that not only the r_2/r_1 ratio is of significance but also the absolute value of r_1 .

The so-called "core" flames (4) are readily qualitatively explainable in terms of the present results, although the published data are not sufficiently detailed to allow a quantitative treatment. Inasmuch as r_1 and y_1 are independent of pressure variations in the reaction zone, the values of k_p should remain also pressure independent. The "core" flames, however, were characterized by a large pressure dependence of the calculated values of k_p , this dependence being more pronounced for faster reactions. In view of variation of D_p with pressure, z_∞ has also to be varied to maintain the flame size and as a result x_1 and therefore also K will be altered leading, in turn, to a drift in the values of δ and of k_p . With increasing pressure, D_p becomes smaller and, therefore, z_∞ is also reduced (for the same C) making x_1 smaller and K larger, and as a result k_p will decrease. This will be noticeable in the case of very fast reactions when x_1 is small and quite sensitive to variations in z_∞ and when δ is large. A change in experimental conditions leading to an increase in x_1 (and a decrease in K and δ) will tend to reduce the pressure dependence. These conclusions are in agreement with the drifts observed by Haresnape, Stevels, and Warhurst (4) and with the necessary change in experimental conditions intuitively inferred by these authors in order to eliminate the pressure dependence of k_p .

Deviations in the Concentration Pattern Method

The deviations from the exponential solution in the concentration pattern method are shown in Figs. 5-8. It is evident that they are on the whole considerably smaller than in the two-point boundary method and for a considerable range of experimental conditions they are practically negligible. This result is in agreement with the view expressed by Smith (8). Only for some quite large values of K the deviations could become appreciable. In this case, the evaluated rate constants would appear smaller than they actually are, and any pressure dependence would be such that with an increasing pressure the rate constants evaluated to the exponential approximation would decrease. Here

again the smaller the absolute value of r_1 the smaller is K , and, consequently also the deviations. The necessity of selection of very small nozzle radii in the experiments of Garvin and Kistiakowsky (3) is, thus, well understandable.

Evaluation of r_1 and y_1

The solutions [8] are independent of the particular values which r_1 and y_1 may have and the foregoing results are, therefore, quite general. However, the constant A_p in Equation [2] which involves r_1 and y_1 has to be known for the calculation of k_p . The value of r_1 is also required for the quantitative evaluation of the deviation factor δ and of eventual deviations in the concentration pattern method.

Two distinct ways of assessing the values of these quantities have been suggested. Hartel and Polanyi (5) assumed that $r_1 = r_n$, where r_n is the radius of the nozzle, and $y_1 = y_n = y_s$, where y_s and y_n are the respective concentrations of the nozzle reactant in the saturator and in the nozzle. Hartel-Polanyi's boundary condition at the origin was used exclusively until very recently when Garvin and Kistiakowsky (3) proposed to assess the value of A_p by setting the consumption of the nozzle reactant in the reaction zone equal to the strength of the assumed point source of this reactant (expressed as the quantity introduced in unit time). Garvin-Kistiakowsky's boundary condition has been used further by Reed and Rabinovitch (7) and by Smith (8). The respective values derived by these authors differ somewhat between themselves. The treatment given by Smith is of particular interest since it is based on the extended theory of spherical diffusion (1) and takes into account the depletion of the atmosphere reactant. It leads to the results

$$[11] \quad r_1 = \frac{v_n r_n^2}{4D_s}, \quad y_1 = y_n \frac{D_s}{D_p}, \quad A_p = \frac{v_n r_n^2}{4D_s} y_n \exp(C_p r_1),^*$$

where v_n is the streaming velocity of the gases in the nozzle.

The introduction of Garvin-Kistiakowsky's boundary condition and the subsequent work by Reed and Rabinovitch and by Smith represent a highly interesting new approach. At the same time, the importance of the distorting effect of the stream of the carrier gas leaving the nozzle, which tends to keep z away from the nozzle, is not yet fully understood. Smith thus proposes also an alternative way of normalizing the exponential solution (the first approximation of the general solution) to allow for the fact that depletion of y by reaction is insignificant inside some radius *not smaller* than r_n because of the effect of the jet. It is also likely that the physical conditions at the nozzle impose some upper limits on y_1 and r_1 , such as $y_1 < y_n$ and $r_1 < r_n$, since at sufficiently high v_n a transition to "cylindrical flames" takes place. In view of this, it is possible that in much of the classical diffusion flame work, where larger nozzle radii were employed, the Hartel-Polanyi boundary conditions were valid to a good approximation. Use of smaller nozzle radii offers the advan-

*In the original treatment the factor $1/4$ appears to have been omitted accidentally and this value is given as $(v_n r_n^2/D_s) y_n \exp(C_p r_1)$. The value for y_1 is not given explicitly.

tage of smaller deviations from the exponential solution and may be preferable for that reason and because of a smaller interference with the assumed rigorously spherical symmetry. The effect of a variation of the nozzle radius, however, ought to be subjected to a critical experimental study on the basis of the foregoing conceptions. The concentration pattern method, on the other hand, is largely free from any uncertainties and, inasmuch as it may prove experimentally feasible to extend it to sodium atom reactions by a suitable modification of the optical method, it could provide a valuable variant of the classical technique.

While the computations reported in the present article were in progress, Smith (8) succeeded in solving in terms of a tabulated function by successive approximations the second order non-linear differential equation of spherical diffusion derived by Cvetanović and LeRoy (1). In the region of its convergence the series representing this solution should yield results identical with the present after allowance is made for the particular boundary conditions adopted by this author.

ACKNOWLEDGMENT

The author is thankful to Prof. C. C. Gotlieb, Dr. Beatrice H. Worsley, and Mrs. Mary Burgess of the Computation Centre, University of Toronto, for the numerical solutions of the reported cases, and to Dr. J. F. Hart for assistance in the organization of the numerical processing of the data for the purpose of the present article. The author is indebted to Prof. D. J. LeRoy for his continued interest and encouragement.

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THE PARTIAL SEPARATION OF Na^{22} FROM Na^{24} BY ION EXCHANGE CHROMATOGRAPHY¹

BY R. H. BETTS, W. E. HARRIS,² AND MARGARET D. STEVENSON

ABSTRACT

Mixtures of the radionuclides Na^{22} and Na^{24} , as the chloride salts, have been partially separated by chromatographic methods. A column 102 cm. in length containing the cation exchange resin Dowex 50 was used. The eluant was 0.7 *M* hydrochloric acid. Na^{22} is held more strongly by the resin than is Na^{24} . The most effective separations were obtained at 25°C. and 5.5°C.; experiments at 48°C. and 68°C. showed much smaller isotope effects.

INTRODUCTION

The separation of isotopes by ion exchange chromatography was first demonstrated by Taylor and Urey in 1938 (15). These workers obtained partial separation of Li^6 from Li^7 , and K^{39} from K^{41} , by elution from a column 30 ft. in length. A naturally occurring zeolite was used as an ion exchange material. Subsequently, partial separations of Li^6 from Li^7 and Ca^{45} from Ca^{48} have been obtained by other workers with synthetic cation exchange resins (7, 9, 11). Very recently, a note has appeared describing the separation of nitrogen isotopes by elution of NH_4^+ from a column of Dowex 50 effectively 600 ft. in length (13). In this work, the nitrogen in the trailing edge of the elution band contained 74% N^{15} ; the ratio $\text{N}^{15}/\text{N}^{14}$ in the starting material was 0.365%, i.e. the natural abundance ratio. This is a very striking result.

In the present work we report experiments relating to the partial separation of 2.7 yr. Na^{22} from 15.0 hr. Na^{24} using the cation exchange resin Dowex 50. This system was chosen for study because the 9% difference in mass between Na^{22} and Na^{24} made it a priori a particularly favorable case in which to observe isotopic separation. An added attractive feature of this isotope pair is that the ratio of Na^{24} to Na^{22} in a given solution can be determined very precisely by radiochemical methods. This technique was in fact used earlier in an unsuccessful attempt to separate these nuclides by elution with ammonium citrate from a 207 cm. Dowex 50 column (4).

Our choice of experimental conditions was based on the following considerations: (i) Sodium ion in aqueous solution does not form complexes with any known anion; there appeared to be no advantage, therefore, in using such eluting agents as citrate or lactate, which have been used with marked success in separating adjacent lanthanide or actinide elements. (ii) Hydrochloric acid was chosen as the eluant mainly because of its experimental convenience. The particular concentration used (0.7 *M*) was chosen to give a K_D of about 8. (K_D is a dimensionless quantity given by the ratio: moles Na^+ per gram of resin/moles Na^+ per gram of solution, and describes the equilibrium distribution of sodium ion between the resin and the liquid phase.) A theoretical

¹Manuscript received September 29, 1965.

Contribution from the Chemistry and Metallurgy Division, Atomic Energy of Canada Limited, Chalk River, Ontario. Issued as A.E.C.L. No. 258.

²Present address: Department of Chemistry, University of Alberta, Edmonton, Alberta.

analysis by Glueckauf (6) shows that for the size of resin particle used in the present work, increases in K_D beyond 8 or 10 have very little effect on the efficiency of the separation obtained. (iii) The flow rates chosen were in general the maximum which could be used while maintaining the column under near equilibrium conditions. Our criterion here was the shape of the elution curve; excessively high flow rates gave a markedly asymmetrical elution curve with a long tail. We have also made use of a theoretical analysis of this aspect (6) which indicated that the flow rates chosen were sufficiently low to obtain maximum efficiency of separation. (iv) The particle size of the resin has a profound effect on the separation achieved by a given length of column, maximum efficiency being obtained with minimum particle diameter. In this work we have used resin with the smallest available particle size.

EXPERIMENTAL

The resin used was 240–400 mesh Dowex 50 in the hydrogen form. After a preliminary purification (1), a small fraction of more uniform size was separated by elutriation with water. The average diameter of particles of this fraction was 25 microns, with 90% in the range 20 to 40 microns. The air dried resin had a capacity of 3.54 meq. of exchangeable hydrogen per gram.

The column was a Pyrex tube 0.90 cm. I.D., 107 cm. in length. It was jacketed with a second column, through which water at the required temperature was circulated from a constant temperature reservoir. The bottom of the column was sealed to a short capillary tube, without stopcock, to minimize dead space between the end of the resin bed and the exit from the column. The column, when operating, contained 36 gm. of resin in 102 cm., and 44 ml. of hydrochloric acid. The top 5 cm. was left free of resin to allow the eluting agent to attain the required temperature before it reached the top of the resin bed. Before each experiment, the resin was conditioned for one day by elution with 0.7 *M* hydrochloric acid.

Na^{23} was supplied as Na^{23}Cl in dilute hydrochloric acid through the courtesy of Mr. R. C. Hawkins of these laboratories. It was purified before use by elution with dilute acid from a separate 60-cm. column of Dowex 50. The specific activity of this material was 25 $\mu\text{c.}$ per mgm. of Na^{23} , i.e., $\sim 4 \times 10^{-4}$ atom % Na^{23} .

Na^{24} was prepared by irradiation of 1 mgm. quantities of analytical reagent sodium carbonate in the Chalk River NRX reactor. It was converted to Na^{24}Cl by evaporation with dilute hydrochloric acid. The specific activity at the start of an experiment was about 2 mc. per mgm. of Na^{23} , corresponding to 2×10^{-3} atom % Na^{24} .

The eluant, 0.7 *M* hydrochloric acid, was prepared by dilution of reagent grade acid with doubly distilled water.

Procedure

Solutions of Na^{23}Cl and Na^{24}Cl were mixed in the required proportions, and the mixture evaporated to dryness twice with dilute hydrochloric acid to ensure that the two radionuclides were in equivalent chemical form initially.

The resulting residue (which amounted to about 3 mgm. of sodium chloride) was dissolved in water, and a portion set aside for later analysis. The remainder was adsorbed on 0.2 gm. of resin, and the resultant slurry transferred to the top of the column. When this added resin had settled in a thin layer, the supernatant water was replaced with 0.7 *M* hydrochloric acid, and the top of the column connected to an overhead reservoir of eluant. The rate of flow of liquid through the column was maintained constant to $\pm 5\%$ by applying a suitable hydrostatic pressure to the top of the column. Provision was made for removing dissolved air from the acid before it entered the column.

Up to 40 consecutive fractions of effluent containing sodium were collected. Samples were prepared from these fractions for measurement of the relative isotopic ratio $\text{Na}^{24}/\text{Na}^{23}$ (see below). For fractions very close to either end of the elution band, 15–20 ml. of solution were used to obtain a sufficient amount of activity. This volume was evaporated to dryness and most of the sodium removed from the traces of resin left behind by extraction with small volumes of water. Finally this aqueous extract was evaporated in a central depression on a copper tray. For most of the fractions, this preliminary concentration was unnecessary, and 0.05–0.5 ml. samples were evaporated directly on the copper trays.

Estimation of the Relative $\text{Na}^{24}/\text{Na}^{23}$ Atom Ratio

The method used depends on measurement of the disintegration rate of a sample when both nuclides contribute about equally to the observed activity, followed by a second measurement after most of the Na^{24} had decayed, leaving only Na^{23} activity. It may be useful to point out here that the initial value of the atom ratio $\text{Na}^{24}/\text{Na}^{23}$ in each run has no "natural" value, and moreover, in a given solution containing these nuclides, this ratio decreases by a factor of two every 15.04 hr. Nevertheless, for any sample this ratio may be given a definite value *referred to a fixed time*. In the following we measure not the absolute atom ratio, but a quantity which is directly proportional to it, viz., the ratio of counts per minute (c.p.m.) from Na^{24} to the corresponding quantity for Na^{23} . We define this ratio as N^{24}/N^{23} .

The relative radioactivity of each sample was measured in a fixed and reproducible geometrical arrangement with a 3 in. NaI-Tl crystal scintillator, coupled optically to a photomultiplier tube (RCA-5819). The crystal and photomultiplier were mounted inside 3 in. of lead shielding. The output from the tube was fed into a scaling circuit and mechanical register. After the Na^{24} in the sample had decayed to about 1% or less of its initial activity, the sample was remeasured.

The method of calculation of the relative isotopic ratio from such data is illustrated below.

At time T_1 let N_1 be the observed c.p.m. for a given sample. Then $N_1 = N_1^{24} + N_1^{23}$, where N_1^{24} and N_1^{23} are the c.p.m. in the sample arising from Na^{24} and Na^{23} , respectively.

Similarly, at time T_2 :

$$N_2 = N_2^{24} + N_2^{23}.$$

Since the half-life of Na^{22} is long relative to periods of time dealt with here, then

$$N_1^{22} \simeq N_2^{22},$$

and

$$\begin{aligned}\Delta N &= N_1 - N_2 = N_1^{24} - N_2^{24} \\ &= N_2^{24} [\exp(0.693 \Delta T/15.04) - 1],\end{aligned}$$

where ΔT (in hours) = $T_1 - T_2$, and 15.04 is the half-life of Na^{24} in hours (10).

If we let

$$\exp(0.693 \Delta T/15.04) = f,$$

then

$$N_2^{24} = \Delta N / (f - 1),$$

and

$$[1] \quad \frac{N_1^{24}}{N_1^{22}} = \frac{N_1 - N_2 + [\Delta N / (f - 1)]}{N_2 - [\Delta N / (f - 1)]},$$

which is the required result.

Since $(f - 1)$ was generally of the order of 80 to 300 ($\Delta T = 95$ to 125 hr.), the terms in f in Equation [1] represent small corrections to this ratio.

Finally, N_1^{24} for each sample in a run was adjusted to some common time in the vicinity of T_1 in the usual way. For this purpose, the half-life of Na^{24} was taken as 15.04 hr. (10).

In the foregoing we neglected the radioactive decay of Na^{22} which occurred during the time ΔT (4-6 days). While this procedure would lead to a 0.3 to 0.4% error in the calculation of *absolute* isotopic abundance, these errors cancel in the present case, since we are interested only in variations in the relative abundance among different samples for which ΔT was effectively constant.

Precision of the Measurement of N^{24}/N^{22}

As will be apparent from the results presented later, a maximum variation of 10% was observed in the ratio N^{24}/N^{22} between the leading and trailing edges of the sodium elution curve in a given run. We feel therefore that it is necessary to outline in rather more detail than is customary further particulars of the counting techniques used, and the precautions taken to minimize errors.

A sufficient number of counts were recorded for each sample to reduce the probable statistical error in the ratio N^{24}/N^{22} to $\pm 0.2\%$. Corrections were made when required for variations in the counting rate of a standard sample (Na^{22}) and for background. Coincidence corrections were applied when necessary. To make this latter correction, the dead time of the counter was measured with paired sources (5, p. 213) of both Na^{22} and Na^{24} , at counting rates comparable with those encountered in the present work. Systematic errors arising from uncertainties in the dead time were minimized by preparing, whenever possible, all comparable sources with nearly equal counting rates. To further reduce the effects of drifts in the counting equipment, the samples in each run were measured in a random progression, viz., the chronological order of counting the samples did not correspond to the order in which these samples came off the column. In addition, samples of the initial solution were measured at irregular intervals during the time in which the samples of effluent from the column were being assayed. Such a procedure served as a secondary "internal" standard to the whole scheme of radioassay.

Since a ratio of counting rates at two times for a given sample is involved, the precision of the method is unaffected by pipetting errors, and more generally does not depend on quantitative transfers at any stage of sample preparation. For the same reason, errors due to slight variations in geometry from one sample to another are also mainly self-cancelling. Errors arising from variable self-absorption in the sources were also negligible because the counting arrangement responded only to γ -rays. In any event, the sources were essentially weightless.

As a measure of the reproducibility of the counting technique, we record below (Table I) typical results for the ratio N^{24}/N^{23} for triplicate samples of the initial solutions in each of three experiments.

TABLE I
VALUES OF N^{24}/N^{23} FOR TYPICAL STOCK SOLUTIONS

Sample No.	Run No.		
	11	12	13
1	1.227	1.889	4.245
2	1.228	1.884	4.251
3	1.230	1.885	4.233
Average	1.228 ± 0.001	1.886 ± 0.003	4.241 ± 0.007

Another more general test of the counting methods was to assay a series of synthetic mixtures of $\text{Na}^{23} + \text{Na}^{24}$ which were prepared by mixing together weighed portions of solutions of each of these nuclides. A comparison of the observed and calculated values of the ratio N^{24}/N^{23} for these mixtures is given in Table II.

TABLE II
MEASUREMENTS OF N^{24}/N^{23} FOR SYNTHETIC SOLUTIONS

Solution No.	N^{24}/N^{23}	
	Obs.*	Calc.
1	0.980 ± 0.003	0.979
2	0.996 ± 0.002	0.994
3	1.023 ± 0.003	1.019
4	1.035 ± 0.003	1.039
5	1.055 ± 0.003	(1.055)†
6	1.074 ± 0.002	1.072

*Average of two values.

†Fitted value.

The results in Tables I and II suggest that the probable error in estimation of N^{24}/N^{23} does not exceed $\pm 0.4\%$.

RESULTS

1. General Features of the Elution of Sodium Ion

Fig. 1 is a typical elution curve obtained in this work. This result is for Run 13 at 24.8°C . (See Tables III and V below.) The elution curves for other runs did not differ markedly from that shown in Fig. 1, although the curves

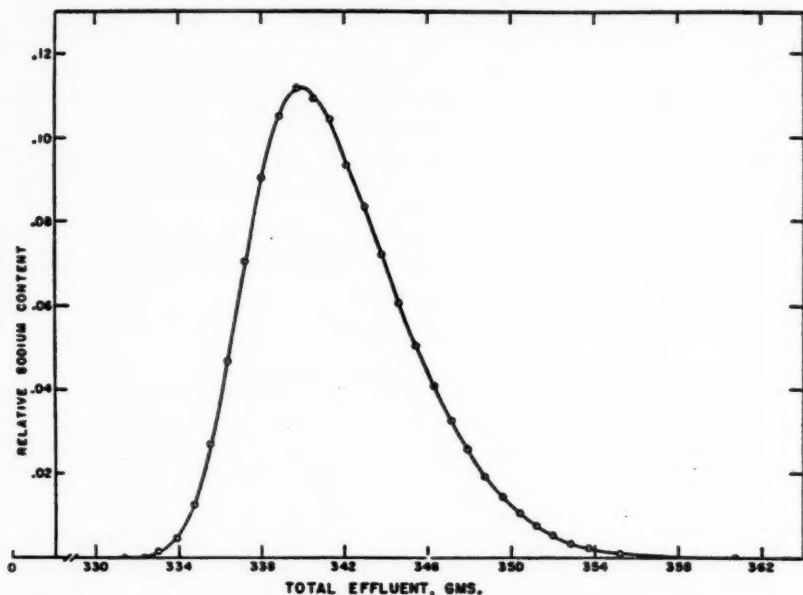


FIG. 1. Sodium elution curve for Run 13 at 24.8°C.

obtained at 5.5°C. showed a longer tail than those at higher temperatures. The position of the maximum decreased with increases in temperature, occurring at 400 ± 5 gm. of eluant at 5.5°C., and at 290 gm. at 67.8°C. These shifts in position of the maximum are presumably caused by corresponding changes in the distribution coefficient of sodium ion between resin and solution. The magnitude of the change agrees with other measurements in the literature on the enthalpy change associated with the sodium-hydrogen exchange on Dowex 50 (3).

It was thought of interest, in passing, to calculate by standard methods (12, p. 190) the number of theoretical plates in the column. The position and width of the elution curve shown in Fig. 1 leads to a value of 10,000 theoretical plates, i.e., 100 per cm. of column length. For comparison, calculations based on physical parameters like particle size, flow rate, etc., according to Glueckauf's treatment of ion exchange chromatography (6) gave a value of 218 plates per cm. In a private communication, Glueckauf and Kitt (8) suggest that allowance should be made in the latter calculation for "wall" effects which cause a curvature in the advancing boundary of the elution band. Their experimental studies of this phenomenon point to a value of 100 to 120 plates per cm. for the flow rate and particle size used in the present study. This is in good agreement with the experimental value of 100 plates per cm. quoted above.

2. Separation of Na^{24} from Na^{23}

Table III summarizes the main results of the present investigation. The items listed are self-explanatory, except for (i) " $(N^{24}/N^{23})_{\text{total}}$ in effluent" and

(ii) "Maximum separation, %". With respect to (i), the c.p.m. of Na²² and of Na²⁴ in each fraction were calculated from the volume of the fraction, the total activity per ml., and the measured ratio N^{24}/N^{22} for each fraction. The total amount of both Na²⁴ and Na²² in the effluent as a whole was calculated from these data. The ratio of these amounts is designated as $(N^{24}/N^{22})_{\text{total}}$ in Table III. The value of this ratio for each run agrees with N^{24}/N^{22} determined on aliquot portions of the corresponding stock solution before its passage down the column. This agreement is a further check on the experimental procedures, and, in addition, is indirect evidence that radioactive nuclides other than Na²² and Na²⁴ were absent in the stock solutions. The "maximum separation" (ii) referred to in Table III was calculated from

$$\frac{(N^{24}/N^{22})_{\text{max}} - (N^{24}/N^{22})_{\text{min}}}{(N^{24}/N^{22})_{\text{stock}}} \times 100\%.$$

Table III shows that at 5.5°C. and 25°C., significant enrichment of Na²² occurred in the leading fractions, and depletion of Na²⁴ in the trailing fractions. The separation of Na²² from Na²⁴ is unquestionably less at 48° and 68°C., and may well be zero.

TABLE III
SUMMARY OF DATA

	Run No.							
	9	10	11	12	13	5	4	8
Temperature, °C.	5.5	5.5	5.5	5.5	24.8	24.9	48.4	67.8
Flow rate, gm./min.	0.11	0.055	0.11	0.10	0.14	0.15	0.27	0.10
N^{24}/N^{22} stock solution*	2.318	0.496	1.228	1.886	4.24	6.44	5.35	4.68
$(N^{24}/N^{22})_{\text{total}}$ in effluent	2.33	0.495	1.219	1.884	4.24	6.41	5.35	—
Maximum N^{24}/N^{22} , leading fraction	2.40	0.510	1.290	1.975	4.43	6.72	5.38	4.70
Minimum N^{24}/N^{22} , trailing fraction	2.15	0.461	1.190	1.824	4.09	6.27	5.25	4.53
Maximum separation, %	10	10	8	8	8	7	2	3

*Average of three values.

To amplify the results in Table III, we list in Tables IV and V the relative isotopic analyses for all samples collected in each of two experiments. These tables show that the central fractions, corresponding to those near the peak in Fig. 1, emerge from the column essentially unchanged in isotopic composition. Only the leading and trailing fractions show significant changes in the atom ratios.*

*The slight rise in N^{24}/N^{22} in the last 0.5 to 1% eluted, shown in Table IV, was noted in several other runs, particularly those at 5.5°C. We believe this effect could arise, for example, by adsorption of traces of sodium on the glass surfaces of the column, followed by a slow removal by the eluting agent. Such effects would tend to cancel any isotopic separation. Similar behavior has been observed in the separation of americium from curium. These elements appear in the effluent in two distinct, well-separated peaks; nevertheless, the last 1 to 2% of material eluted contains both americium and curium (2).

TABLE IV

DATA FOR RUN 12 AT 5.5°C.

Initial $N^{24}/N^{22} = 1.886 \pm 0.003$ (see Table I)

Fraction Na eluted	N^{24}/N^{22}	Fraction Na eluted	N^{24}/N^{22}
0-0.0018	1.975	0.774-0.810	1.858
0.0018-0.0059	1.966	0.810-0.842	1.845
0.0059-0.0191	1.941	0.842-0.869	1.851
0.0191-0.045	1.933	0.869-0.892	1.834
0.045-0.088	1.930	0.892-0.911	1.828
0.088-0.146	1.927	0.911-0.928	1.841
0.146-0.216	1.917	0.928-0.941	1.824
0.216-0.292	1.902	0.941-0.953	1.820
0.292-0.369	1.899	0.953-0.960	1.842
0.369-0.442	1.888	0.960-0.967	1.832
0.442-0.513	1.892	0.967-0.976	1.831
0.513-0.576	1.878	0.976-0.982	1.838
0.576-0.635	1.877	0.982-0.989	1.838
0.635-0.687	1.885	0.989-0.996	1.862
0.687-0.734	1.853	0.996-0.998	1.873
0.734-0.774	1.849	0.998-1.000	1.870

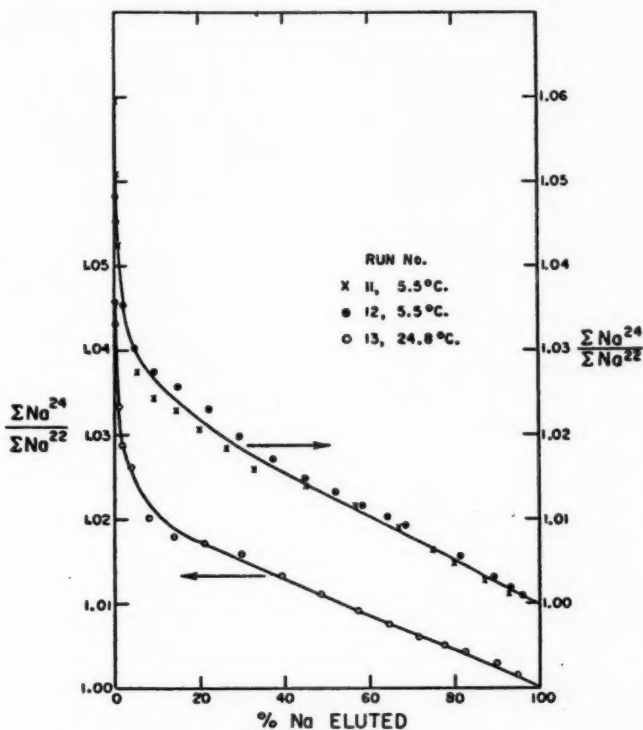
TABLE V

DATA FOR RUN 13 AT 24.8°C.

Initial $N^{24}/N^{22} = 4.243 \pm 0.007$ (see Table I)

Fraction Na eluted	N^{24}/N^{22}	Fraction Na eluted	N^{24}/N^{22}
0. -0.0004	4.433	0.770-0.821	4.213
0.0004-0.0017	4.422	0.821-0.862	4.190
0.0017-0.0056	4.370	0.862-0.896	4.177
0.0056-0.016	4.356	0.896-0.923	4.176
0.016-0.038	4.347	0.923-0.944	4.140
0.038-0.077	4.310	0.944-0.960	4.144
0.077-0.135	4.306	0.960-0.972	4.154
0.135-0.209	4.312	0.972-0.981	4.119
0.209-0.296	4.296	0.981-0.987	4.092
0.296-0.388	4.266	0.987-0.992	4.099
0.388-0.479	4.251	0.992-0.994	4.129
0.479-0.565	4.236	0.994-0.996	4.111
0.565-0.642	4.222	0.996-0.999	4.108
0.642-0.711	4.215	0.999-1.000	4.133
0.711-0.770	4.221		

A useful way of displaying such results is to plot $\Sigma Na^{24}/\Sigma Na^{22}$ vs. % elution of sodium. The Σ refers to the cumulative fraction of Na^{24} or Na^{22} in the effluent from the beginning of the elution. Fig. 2 shows such plots for several runs. The meaning of these curves is best illustrated by example. In Runs 11 and 12 (upper curve in Fig. 2), an enrichment of 1.4% in Na^{24} relative to Na^{22} would be obtained by collecting the first 50% of the effluent, and a 2.6% enrichment if the first 10% of the sodium is collected. Successively higher enrichments are obtained as the % of total sodium eluted approaches a value of zero.

FIG. 2. Enrichment of effluent in Na^{24} .

DISCUSSION

An analysis of the results at 5.5°C. indicates that the peak of the Na^{24} curve is reached about 0.05 to 0.07 ml. earlier than the peak for Na^{22} . If the observed separation is ascribed solely to differences in K_D between the two nuclides, then this result implies that K_D for Na^{24} is 1 part in 6000 smaller than K_D for Na^{22} . This small difference presumably represents the net result of isotope effects on at least two equilibria: (i) the interaction of sodium ion with water molecules of the hydration sphere, and (ii) the reaction of the hydrated ion with the resin. In this connection it is pertinent to note that experiments with H_2O^{16} - H_2O^{18} mixtures have revealed isotope effects in the hydration of chromium (III) and certain other cations (14).

A further point of interest is the virtual absence of separation at 48° and 68°C. The distribution of sodium ion between the resin and acid is not markedly temperature sensitive (3); it is unlikely, therefore, that the difference in the temperature coefficients for the distribution of these nuclides would be sufficiently large to cancel out the isotope effect at 48°C., when it is clearly observable at 5° and 25°C. This absence of separation at higher temperatures may be due to convective mixing of the elution band due to slight temperature

gradients in the system, or possibly to mixing caused by formation of bubbles at these temperatures. Although, as indicated earlier, precautions were taken to reduce such effects, further work with more careful attention to these points would be desirable.

A comparison of the present results with those referred to earlier (7, 9, 11, 13, 15) shows that on Dowex 50 the heavier nuclide is less firmly held by the resin for the pairs $\text{Li}^6\text{--Li}^7$ and $\text{Na}^{22}\text{--Na}^{24}$. The behavior of $\text{N}^{14}\text{--N}^{15}$ is reversed, N^{15} being more strongly retained by the resin than is N^{14} . While perhaps not strictly comparable, the separation of K^{39} from K^{41} obtained with zeolitic (inorganic) material showed that the lighter isotope comes off the column first (15). The same trend is evident for the $\text{Ca}^{40}\text{--Ca}^{45}$ separations, i.e., the lighter nuclide comes off the column preferentially (11). This result is also probably not comparable with the lithium and sodium studies, since a complexing agent (ammonium citrate) was used as an eluting agent. However it is clear that the order of elution of members of isotopic pairs in the mass range 6 to 45 is not a simple function of the relative masses of the nuclides involved. Further studies of other isotopic pairs above calcium, e.g., $\text{Fe}^{54}\text{--Fe}^{59}$, would be useful in this connection. Parallel studies of isotope effects concerned in complex ion formation would also be instructive.

ACKNOWLEDGMENTS

We should like to thank R. C. Hawkings for providing the Na^{22} used in this work. The assistance of J. E. Hardy in developing alternative radiochemical methods for assay of $\text{Na}^{24}\text{--Na}^{22}$ mixtures is gratefully acknowledged. We are indebted to E. Glueckauf for permitting us to refer to his work before publication; we also acknowledge very useful private correspondence with E. Glueckauf and G. P. Kitt.

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AN ISOTOPIC STUDY OF THE REDUCING ACTION OF THE GRIGNARD REAGENT¹

By G. E. DUNN AND JOHN WARKENTIN²

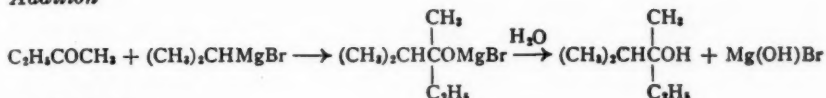
ABSTRACT

Benzophenone has been reduced to benzhydrol with three samples of isobutylmagnesium bromide containing deuterium in the *alpha*, *beta*, and *gamma* positions, respectively. Deuterium was found only in the benzhydrol obtained from β -deuteroisobutylmagnesium bromide. Comparison of the ratios of deuterium to protium in β -deuteroisobutylmagnesium bromide and in the benzhydrol obtained from it shows an isotope effect of about two. In the decarboxylation of hydroxyl-deuterated dimethylmalonic acid an isotope effect of 4.5 was observed. These results are considered in terms of the probable mechanisms of the reactions.

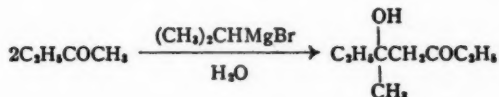
INTRODUCTION

Of the many reactions of the Grignard reagent, the most familiar and probably the most used is the addition to a carbonyl group. It has long been known, however, that this reaction is frequently complicated by side reactions which may replace some or all of the addition. The three most important of these side reactions are commonly referred to as condensation, enolization, and reduction (8). They are illustrated below in terms of methyl ethyl ketone and isopropylmagnesium bromide (15).

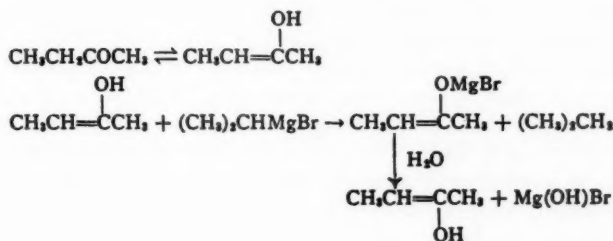
Addition



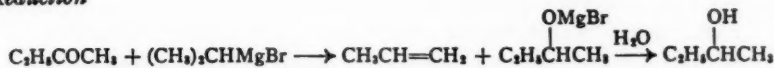
Condensation



Enolization



Reduction



¹Manuscript received September 12, 1955.

Contribution from the Chemistry Department of the University of Manitoba, Winnipeg, Manitoba. This paper was presented at the May, 1955, meeting of the Chemical Institute of Canada at Quebec City, Quebec.

²Holder of a National Research Council Bursary, 1954-55.

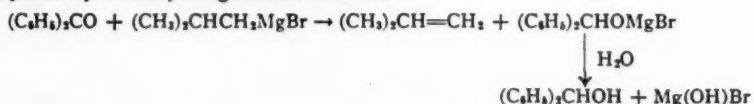
The condensation reaction is, at least formally, analogous to the common base-catalyzed aldol condensation with the Grignard reagent as the base, and the enolization reaction is an example of the well-known tendency of the Grignard reagent to react with acidic hydrogen. The reduction reaction, however, shows a property of the Grignard reagent which is not illustrated among its better known reactions and, consequently, this side reaction has attracted more interest and experiment than the other two.

The equation written above for the reduction reaction indicates that the Grignard reagent is converted into olefin, and careful work by Noller, Grebe, and Knox has shown that, at least in the reduction of benzophenone by isobutylmagnesium bromide, the amounts of olefin and alcohol produced are exactly equivalent (14). It is also commonly observed that the double bond of the olefin has for one of its carbon atoms that one to which magnesium was originally attached. For example, γ -phenylpropylmagnesium bromide when used as a reducing agent is converted into allylbenzene (2). Evidently the net result of the reaction is the elimination of magnesium and hydrogen from adjacent carbon atoms. This conclusion is supported by the observation that, although the amounts of all three side reactions increase with increasing branching in the alkyl groups of both carbonyl and Grignard reagents, reduction does not occur when the Grignard does not contain a hydrogen atom on the carbon *beta* to magnesium (20).

Although the evidence considered above shows that the over-all result of the reduction is the transfer of the elements of magnesium halohydride from Grignard reagent to carbonyl compound, it does not, of course, prove that a hydrogen atom originally attached to the β -carbon of the Grignard is the one actually transferred to the carbonyl compound. It is conceivable that the actual hydrogen atom appearing in the carbinol product could come from the α - or γ -position of the Grignard reagent, from the solvent, or from the water used in the hydrolysis. However, in the absence of evidence to the contrary, attempts to devise a mechanism for the reduction have naturally been based on the simplest reasonable assumption: namely, that a hydride ion is transferred directly from the Grignard molecule to the carbonyl compound.

The objects of the present investigation have been: first, by substituting deuterium for hydrogen in various positions of the Grignard molecule to determine whether or not the hydrogen atom lost from the β -position of the Grignard reagent is, in fact, the one which appears in the carbinol product of the reduction; and, second, by observing the isotope effect in the hydrogen transfer to learn something about the sequence and relative speeds of the various steps in the reaction.

The reaction we have chosen to study is the reduction of benzophenone to benzhydrol by isobutylmagnesium bromide:



It was chosen for a number of reasons: (a) the ketone cannot undergo condensation or enolization and gives an almost quantitative yield of the reduction

product; (b) this reaction is one of the very few for which it has been demonstrated that the amounts of olefin and alcohol produced are equivalent; (c) the Grignard has hydrogen in the α -, β -, and γ -positions which could, in principle, be transferred to the ketone; and (d) the halomagnesium salt of benzhydrol is insoluble in ether so that it can readily be separated from unreacted benzophenone and other reaction products, if any.

Three samples of isobutylmagnesium bromide were prepared which contained deuterium in the α -, β -, and γ -positions respectively. Benzophenone was reduced by each of these, using two equivalents of Grignard reagent to one of benzophenone. By analyzing the resultant benzhydrol samples for deuterium it could be determined whether or not hydrogen is transferred from the Grignard reagent and, if so, from which position in it. By comparing the deuterium to protium ratios in the Grignard reagent and in the benzhydrol obtained from it the isotope effect in the reaction could be determined.

EXPERIMENTAL

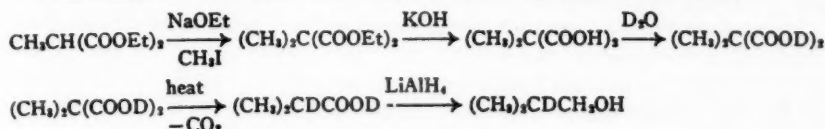
The deuterated Grignard reagents required for this work were prepared from deuterated isobutyl bromides obtained from the corresponding deuterated isobutyl alcohols. A variety of methods for the synthesis of these alcohols were explored, using undeuterated materials. The yields quoted in the procedures described below are those obtained from the undeuterated materials since the small quantities of deuterated compounds used were usually distilled directly into the reaction vessel for the next step in the synthesis without measurement.

α -Deuteroisobutyl Alcohol

This compound was made by reduction of isobutyraldehyde with lithium aluminum deuteride. Isobutyraldehyde (4.2 gm., 0.058 mole) in 20 ml. of dry ether was added dropwise to a stirring solution of 0.65 gm. (0.017 mole) of lithium aluminum deuteride in 20 ml. of ether. A 45 min. reflux period was followed by hydrolysis with dilute hydrochloric acid and extraction of the aqueous layer with ether. The dried ether extracts were evaporated and the residue distilled. The yield of isobutyl alcohol boiling in the range 96–107°C. was 70%.

β -Deuteroisobutyl Alcohol

This compound was synthesized by the following series of reactions:



Methylmalonic acid diethyl ester (26.0 gm., 0.16 mole) was added to a solution of 3.8 gm. of sodium (0.16 gm.-atom) in 100 ml. of absolute ethanol. Then 22.7 gm. (0.16 mole) of methyl iodide was added dropwise. After a three-hour reflux period 2 ml. of methyl iodide was added and refluxing continued for another hour. Ethanol was distilled off and the residue treated with water.

From ether extracts of the aqueous solution there was obtained 9.1 gm. of dimethylmalonic acid diethyl ester boiling at 186–190°C., a yield of 68%.

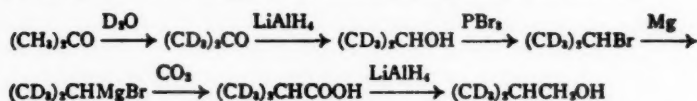
This ester was saponified by refluxing it for 2.5 hr. with an equal weight of potassium hydroxide dissolved in its own weight of water. Unsaponified ester was removed by extraction with ether. Dimethylmalonic acid was isolated by extracting the acidified aqueous solution with ether, evaporating the ether, and crystallizing the residue from benzene. It melted at 188–190°C. Yields were 90% or better. Recrystallization from ether raised the melting point to the literature value of 192–193°C. Neutral equivalent was 67.5 ± 2.0 as compared to calculated values of 66 for dimethylmalonic acid and 59 for methylmalonic acid.

Dimethylmalonic acid (21.5 gm., 0.163 mole) was equilibrated with deuterium oxide by dissolving it in 60 ml. of dioxane (purified by the method of Fieser (4), containing 3.3 gm. (0.165 mole) of heavy water³ and allowing the solution to stand at room temperature for 70 hr. Dioxane and water were removed at 90°C. under reduced pressure, and the residue of deuterodimethylmalonic acid was decarboxylated by heating the distilling flask containing it above 195°C. in an oil bath. The deuterioisobutyric acid which distilled over had a neutral equivalent of 91 ± 2 compared to the calculated value of 89. The over-all yield of exchange and decarboxylation was 85%.

Deuterioisobutyric acid (12.0 gm., 0.14 mole) in 15 ml. of dry ether was added dropwise with stirring to a suspension of lithium aluminum hydride (7.0 gm., 0.14 mole) in 45 ml. of ether. The mixture was refluxed for an hour, then hydrolyzed with water, and acidified. From the ether layer was obtained 6.1 gm., a 60% yield, of β -deuterioisobutyl alcohol, b.p. 96–107°C.

γ -Deuterioisobutyl Alcohol

This compound was prepared by the following series of reactions:



Acetone (30 gm., 0.52 mole) was equilibrated with deuterium oxide (30 gm., 1.5 mole) containing 0.2 gm. of sodium hydroxide. After 48 hr. at room temperature the mixture was distilled through a 9×1.5 cm. column packed with 3 mm. glass helices, distillate being collected up to 95°C. This deuterioacetone was dried over calcium sulphate and filtered.

Deuterioacetone (14.0 gm., 0.24 mole) was dissolved in 20 ml. of dry diethyl carbitol and the solution was added slowly to a suspension of 3.0 gm. (0.08 mole) of lithium aluminum hydride in 20 ml. of diethyl carbitol. At the end of 1.5 hr. the mixture was acidified with dilute hydrochloric acid and distilled, distillate being collected up to 95°C. This distillate was redistilled through a 9×1.5 cm. column packed with 3 mm. glass helices. The yield of deuterioisopropyl alcohol boiling at 79–81°C. was 11.4 gm. (80%).

³Heavy water was obtained from the Commercial Products Division of Atomic Energy of Canada, Ltd., and was reported by the supplier to contain 99.73 atom-% deuterium.

Deuteroisopropyl alcohol was converted to the corresponding bromide, b.p. 56–60°C., in 55% yield by the method described below for converting deuterioisobutyl alcohol to its bromide.

Deuteroisopropyl bromide (24.5 gm., 0.20 mole) was converted to the Grignard reagent with 0.22 gm-atom of magnesium in 60 ml. of dry ether in the usual way. The yield by titration with standard acid was 85%. This was poured into a slurry of crushed Dry Ice in ether; the mixture was acidified and extracted with ether. From the ether extracts was obtained 11.6 gm. (78%) of deuterioisobutyric acid boiling at 145–150°C.

Deuterioisobutyric acid was reduced to γ -deuterioisobutyl alcohol by means of lithium aluminum hydride in ether as described above under β -deuterioisobutyl alcohol. The yield was 65%.

Conversion of Deuterioisobutyl Alcohols to Deuterioisobutyl Bromides

Phosphorus tribromide (19.5 gm., 0.072 mole) was added dropwise with stirring to 12.8 gm. (0.173 mole) of isobutyl alcohol over a period of 45 min. while the reaction was being cooled in an ice-salt bath. The mixture was then distilled, distillate being collected up to 96°C. This distillate was cooled to 0°C., washed with cold concentrated sulphuric acid, cold sodium carbonate solution, and cold water in turn, then dried and distilled. Yields of the various deuterated isobutyl bromides boiling at 88–92°C. ranged from 40% to 50%.

Reduction of Benzophenone by Deuterated Grignard Reagents

The three deuterated isobutyl bromides obtained from the above reactions were diluted with ordinary isobutyl bromide where necessary to give enough material for the subsequent reductions, then analyzed for deuterium. Three reductions with each bromide were attempted. In a typical run 3.0 gm. (0.022 mole) of deuterated isobutyl bromide in 5 ml. of dry ether was added to a 10% excess of magnesium (0.53 gm.) in 25 ml. of dry ether. Reaction was initiated by gentle warming, and completed by refluxing for three hours. Titration with standard acid showed the yield to be 75%. To this solution was added slowly one-half of the equivalent quantity (1.51 gm., 0.0083 mole) of benzophenone dissolved in 10 ml. of dry ether. The solution turned deep red as soon as the ketone was added, but the color disappeared when the addition was complete and the solution had been refluxed for a few minutes. After a few hours of reflux, the bromomagnesium salt of benzhydrol was allowed to settle out, filtered, washed with ether, and hydrolyzed with dilute acid. The liberated benzhydrol was extracted with ether and recrystallized from ligroin. The yield of benzhydrol melting at 66°C. was 1.2 gm. (80%).

Deuterium Analyses

The samples were burned in a standard macrocombustion apparatus using a Vycor tube and a plug of silver wool to trap halogens. The water of combustion was collected in a Dry Ice trap and purified by the method of Keston, Rittenberg, and Schoenheimer (6) except that calcium oxide and potassium permanganate were used instead of chromium trioxide and potassium hydroxide. The density of the water of combustion was determined by the gradient

density tube method described by Anfinson (1). Two gradients were used, one covering the range 0–8% D_2O for samples rich in deuterium and another covering the range 0–2% D_2O for less concentrated samples.

RESULTS

Table I lists the analytical results. The three runs with α -deuteroisobutyl bromide used the same starting material so that the three analyses of α -deuteroisobutyl bromide are, in effect, triplicate analyses of the same material. Thus the three analyses illustrate the reproducibility of the method.

TABLE I
DEUTERIUM ANALYSES

Source of water sample	Run No.	Weight-% D_2O^a	Atom ratio D/H in labelled position
α -Deuteroisobutyl bromide	1	0.70	0.029
	2	0.68	0.028
	3	0.69	0.029
Benzhydrol from α -deuteroisobutyl bromide	1	0.00	0.000
	2	0.00	0.000
	3	0.00	0.000
β -Deuteroisobutyl bromide	1	1.38	0.126
	2	1.48	0.137
	3	—	—
Benzhydrol from β -deuteroisobutyl bromide	1	0.65	0.076
	2	0.78	0.092
	3	—	—
γ -Deuteroisobutyl bromide	1	20.65	0.397
	2	21.32	0.418
	3	—	—
Benzhydrol from γ -deuteroisobutyl bromide	1	0.00	0.000
	2	0.03	0.003
	3	0.00	0.000
α -Deuteroisobutyric acid (dimethylmalonic acid)	1	14.16	1.072
	2	14.41	1.109
	3	14.39	1.107
β -Deuteroisobutyl alcohol	1	3.06	0.382
	2	3.08	0.384
	3	—	—

^aA blank space indicates that a run or analysis was lost by accident.

It is seen from the table that the benzhydrols obtained by reduction of benzophenone with β -deuteroisobutyl Grignard reagents contain deuterium while those obtained from α - and γ -deutero Grignard reagents do not. Therefore, the reduction occurs by hydrogen transfer from the β -position of the Grignard reagent, as has long been supposed.

The fact that the ratio of deuterium to protium in the labelled position of the benzhydrol is less than that in the β -deuteroisobutyl bromide from which

it was obtained indicates that there is an isotope effect in the transfer.⁴ The numerical value of the isotope effect can be calculated from the following considerations. If the reaction is assumed to be first order with respect to Grignard reagent, then

$$k_H t = \ln [a/(a-x)] \quad \text{and} \quad k_D t = \ln [a'/(a'-x')]$$

are the rate expressions for the reactions of normal and deuterio Grignard reagents, respectively, where k_H is the rate constant for the transfer of hydrogen, k_D is the rate constant for the transfer of deuterium, a is the initial concentration of non-deuterated Grignard, a' is the initial concentration of deuterated Grignard, x is the concentration of non-deuterated product at time t , and x' is the concentration of deuterated product at time t . The isotope effect, k_H/k_D , is then given by the expression

$$[1] \quad \frac{k_H}{k_D} = \frac{\log[a/(a-x)]}{\log[a'/(a'-x')]}.$$

If the substitutions $a'/a = A$, $x'/x = X$, and $(x+x')/(a+a') = P$ are made, the above expression becomes

$$[2] \quad \frac{k_H}{k_D} = \frac{\log(1+X) - \log[1+X-P(1+A)]}{\log(1+1/X) - \log[1+1/X-P(1+1/A)]}$$

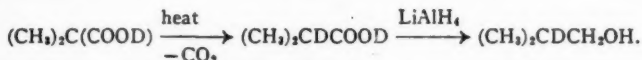
where A is the ratio of deuterium to protium in the labelled position of the reactant, X is the ratio of deuterium to protium in the labelled position of the product, and P is the fraction of reaction completed.

Since purified benzhydrol was isolated corresponding to 80% or more of the benzophenone used in the reactions, it is evident that the reduction of benzophenone must have been close to quantitative. And since two equivalents of Grignard were used to one of benzophenone, the fraction of Grignard reacted is one-half. Using this value for P and the values of X and A from Table I, the isotope effect, k_H/k_D , is found to be 2.0 in Run 1, and 2.2 in Run 2.

Equation [2] can also be used to calculate what fraction of the reduction could have taken place by transfer of hydrogen from the α - and γ -positions of the Grignard without producing a detectable amount (0.01% by weight) of deuterium in the water of combustion from the resulting benzhydrol. If it is assumed that the isotope effect in these hypothetical reductions is six, a value near the maximum allowed by theory and experience (3), then it is found that the maximum per cent of reduction which could have escaped detection is 17% from the α -position and 1% from the γ -position. The value is large in the α -position because a short supply of lithium aluminum deuteride necessitated a low concentration of deuterium in the α -deuteroisobutyl bromide. However, it seems reasonable to suppose that the reaction takes place by one mechanism and not several, and since it is evident that the reduction does involve the β -hydrogen and that not more than 17% of it can involve α -hydrogen, it is highly probable that the reduction takes place by transfer of β -hydrogen exclusively.

⁴That deuterium is not lost from the alkyl groups of alkyl halides or alcohols during formation or hydrolysis of metal derivatives is shown by the work of Shiner (16).

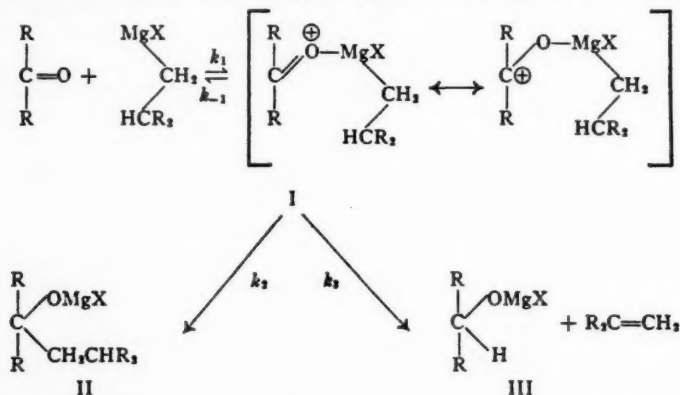
The deuterium analyses on dimethylmalonic acid and β -deuteroisobutyl alcohol can be used to calculate the isotope effect in the decarboxylation reaction



Here it is desired to compare the D/H ratio in the carboxyl groups of dimethylmalonic acid with that on the α -carbon atom of the isobutyric acid obtained from it. Since only carbon dioxide is lost during the decarboxylation itself, the over-all deuterium to protium ratio in the two compounds will be the same. Actually, isobutyric acid was analyzed and the result applied to both acids. Analysis of the isobutyl alcohol obtained from the isobutyric acid gave the D/H ratio on the β -carbon of the alcohol, which should be the same as that on the α -carbon of the isobutyric acid. Use of these ratios in Equation [2] gave a calculated isotope effect, k_H/k_D , of 4.5.

DISCUSSION

A variety of mechanisms have been suggested for the reducing action of the Grignard reagent, and these have been reviewed recently by Kharasch and Reinmuth (8). Probably the most satisfactory of these is the mechanism proposed by Whitmore, or some modification of it. Whitmore proposed (19) that the carbonyl oxygen co-ordinates with the Grignard magnesium forming a six-membered ring complex, I, which can either rearrange to addition products, II, or transfer a hydrogen from the β -carbon of the Grignard to the carbonyl carbon to give reduction products, III. This mechanism of reduction,



or something very like it, is given strong support by the asymmetric reductions accomplished by Mosher and LaCombe (12).

Our experimental results tend to support the Whitmore mechanism since they show that the reducing hydrogen does come from the β -carbon of the Grignard reagent as Whitmore (and many others) proposed. They do not, of course, support or contradict the theory that reduction takes place through hydrogen transfer within a complex. However, if it is assumed that such a complex is involved in the reaction, then our results show that the complex is

in equilibrium with reactants, and that the rate of attainment of equilibrium is greater than the rate of decomposition of complex to reduction products. This is evident from the following considerations. The substitution of deuterium for protium on the β -carbon of the Grignard reagent should have no significant effect on the rate of co-ordination between magnesium and oxygen; hence deuterated and undeuterated complex should be formed in the ratio in which deuterated and undeuterated Grignard reagents were introduced. Then if every complex decomposed into reduction products (in our reaction there were no other products) the ratio of deuterium to protium in the labelled position of benzhydrol would be the same as that in the isobutyl bromide from which it was made. But an isotope effect of about two was observed, so that not every complex can decompose to alcoholate and olefin. That is, k_{-1} in the mechanism scheme above must be greater than k_3 .

An interesting modification of the Whitmore mechanism has been proposed by Swain (17). From a consideration of the order of reactivity of a series of Grignard reagents toward nitriles and carbonyl compounds he concludes that, while reduction takes place by the decomposition of a complex as proposed by Whitmore, addition must take place by attack of a second Grignard molecule on the complex. Support for this theory was found in the observation that when magnesium bromide is added to the carbonyl solution prior to the Grignard reagent the yield of addition product is increased at the expense of reduction (18). This is explained by pointing out that magnesium bromide should be a better complexing agent than the Grignard reagent, and that a complex between carbonyl compound and magnesium bromide would be incapable of reductive hydrogen transfer but would still be subject to attack by a Grignard molecule leading to addition.⁵

McBee, Pierce, and Meyer have shown by a series of vapor pressure measurements in phenetole that magnesium bromide does complex some ordinary aldehydes and ketones, but that no complex is formed with analogous fluorinated carbonyl compounds (11). Since Grignard reagents should complex less readily than magnesium bromide, these authors conclude that reduction of fluorinated carbonyl compounds takes place without intermediate complex formation. Nevertheless, McBee, Pierce, and Higgins have shown that added magnesium bromide favors addition and hinders reduction of fluorinated aldehydes and ketones just as with non-fluorinated compounds (10). This seems to throw some doubt on the interpretation by Swain and Boyles of the mechanism of the action of added magnesium bromide.

However, it may be noted that the vapor pressure measurements on solutions of magnesium bromide and fluorinated carbonyl compounds actually show that the equilibrium concentration of complex is very low, not that no complex is formed. So long as the rate of attainment of equilibrium is fast the

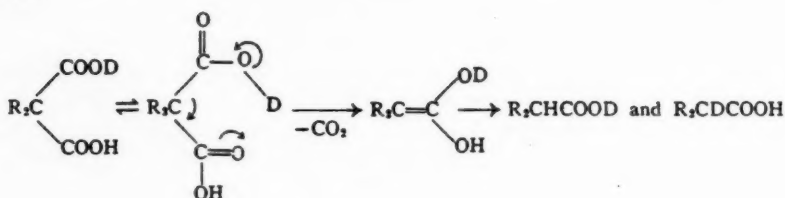
⁵It has long been thought that magnesium halide is also in equilibrium with the Grignard reagent itself (5, 7).



If both $RMgX$ and R_2Mg enter into reaction with carbonyl compound, and if R_2Mg is a better reducing agent (or poorer adding agent) than $RMgX$, then the results of Swain and Boyles can be explained simply by the effect of added magnesium bromide on this equilibrium. Some support, but certainly not proof, is given this alternative explanation by the work of Noller on the reducing action of diisobutylmagnesium on benzophenone (18).

reduction could still take place through a complex even though its concentration were never large. Thus the interpretation of the effect of added magnesium bromide could still be that of Swain and Boyles. The isotope effect observed in the present work shows that if a complex is formed it does reach equilibrium with its components rapidly, at least in the case of benzophenone and isobutylmagnesium bromide. Hence the possibility that Grignard reduction of fluorinated carbonyl compounds takes place through a complex is still open.

The isotope effect observed in the decarboxylation of dimethylmalonic acid throws little light on the mechanism of that reaction. A reasonable mechanism has been proposed by King (9) which predicts the observed isotope effect:



Indeed, the symmetry of the molecule is such that it is difficult to devise a mechanism which does not predict an isotope effect. The fact that one does exist is simply noted in passing.

ACKNOWLEDGMENT

The authors wish to thank the National Research Council of Canada for a grant in aid of this research and for the gift of the lithium aluminum deuteride used in it.

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NOTES

PREPARATION OF D- AND L-GLYCERALDEHYDE FROM KETOHEXOSES*

BY A. S. PERLIN AND CAROL BRICE

When D-fructose is treated in acetic acid with lead tetraacetate two moles of oxidant are consumed rapidly and the reaction then virtually ceases (6, 11). The product of this oxidation, isolated in approximately 90% yield, is a formic acid-glycolic acid diester of D-glyceraldehyde (11). Hydrolysis of the ester groups with dilute acid affords D-glyceraldehyde. L-Sorbose reacts with lead tetraacetate in the same way yielding a formate-glycolate diester of L-glyceraldehyde and finally, by hydrolysis, L-glyceraldehyde. The over-all yield from each ketose, as determined by hypoiodite titration and from the apparent chromatographic purity of the preparations, is 80 to 90% of theory. Each compound has been characterized as its dimedon derivative. Crystalline DL-glyceraldehyde is obtained in 85% yield by oxidation of an equimolar mixture of D-fructose and L-sorbose. This high degree of conversion may be contrasted with that of 16.2% over-all yield from acrolein (9) and of 17.5% from monoacetone glycerol (4).

Freshly prepared, the D- and L-isomers have specific optical rotations, respectively, of $+8.3^\circ$ and -8.6° . According to Baer and Fischer (1), the specific rotation of D- and L-glyceraldehyde is $\pm 14^\circ$ if the compound is first dried *in vacuo* at 55°C . This observation has been confirmed using the currently-described L-glyceraldehyde sample which, after the prescribed treatment, shows an initial specific rotation of -14.3° . The infrared absorption spectra of the D-, L-, and DL-compounds are identical. Absorptions at the carbonyl frequencies are very weak, which agrees with the known tendency of glyceraldehyde to dimerize by forming a hemiacetal linkage between the aldehyde group of one molecule and an hydroxyl group of a second molecule (16, 1). The spectrum of the crystalline DL-dimer differs slightly from that of the same compound as a sirup, and carbonyl bands are absent.

The present results show that the degradative oxidation of ketohexoses provides a facile method for preparing the relatively rare trioses directly from readily available sugars, which may be more advantageous in some instances than the procedures of Fischer and Baer (1, 3). Limited oxidation of D-glucose with periodate, reported recently by Schöpf and Wild (13), constitutes another convenient source of the D-isomer. The preparation of tetroses from aldohexoses and of trioses from aldopentoses has been described elsewhere (10) and is analogous to the present procedure. Oxidation of a pentose, however, is not quite as favorable to the formation of glyceraldehyde as is the degradation of a ketohexose since, with the former, some overoxidation occurs (11),

*Issued as Paper No. 210 in the *Uses of Plant Products Series* and as N.R.C. No. 3797. Presented in part before the 38th Annual Conference of The Chemical Institute of Canada, Quebec City, Quebec, 1955.

the yield of triose is smaller, and traces of pentose and tetrose are also found together with the triose (10). Moreover, D-fructose and L-sorbose are among the least costly of sugars and they are therefore especially desirable as starting materials.

Oxidation of ketohexoses by the reaction described has been suggested (11) as a possible procedure for degrading D-fructose labelled with carbon-14.

EXPERIMENTAL

D-Fructose, L-sorbose, and all solvents were of reagent grade quality. Lead tetraacetate was prepared according to the procedure recommended by Vogel (14), or was obtained commercially (Matheson Co., Inc.), both samples being equally satisfactory.

Solutions were concentrated *in vacuo* at 35–40°C.

D-Glyceraldehyde

D-Fructose (5.0 gm., 0.028 mole) was dissolved in 3 ml. of water* and the solution was diluted with 150 ml. of glacial acetic acid. Lead tetraacetate (12.9 gm. dry weight, 0.059 mole) was added to the solution with vigorous stirring and, 20 min. after the oxidant had dissolved, the lead was precipitated by adding 35 ml. of a 10% solution of oxalic acid in acetic acid. Stirring was continued for a further 20 min. and the suspension was filtered. The filtrate was concentrated to the consistency of a thin sirup and the product was extracted into ethyl acetate, the insoluble lead salts being filtered off. Removal of the ethyl acetate afforded sirupy D-glyceraldehyde formate-glycolate diester, 4.6 gm. (94% yield). The diester (2.3 gm.) was dissolved in 75 ml. of 0.05 N sulphuric acid and the ester groups were hydrolyzed by heating for eight hours at 50°C. Sulphuric acid and the liberated formic and glycolic acid were removed by portionwise addition with vigorous stirring of Dowex-1 resin (200–400 mesh; regenerated with 1 N sodium bicarbonate). The resin was filtered off and washed well on the filter with water. Hypiodite titration (15) indicated that the combined neutral filtrates contained 1.13 gm. of D-glyceraldehyde (89% yield based on D-fructose). The specific rotation of the D-glyceraldehyde in this solution was $[\alpha]_D^{25} + 8.3^\circ$ (c, 0.75).

On paper chromatograms, using ethyl acetate/pyridine/water (8) and methyl ethyl ketone/water (2) as solvents, the product moved at the same rate as L-glyceraldehyde prepared from L-arabinose (10), both compounds exhibiting some streaking. No other sugars appeared to be present, urea oxalate spray (5) being used to test for the presence of fructose. With aniline oxalate spray (7) D-glyceraldehyde gave a deep brown color and under ultraviolet light a mauve fluorescence which faded after a short period. The infrared absorption spectrum, obtained with the potassium bromide window technique (12), was identical with that of L-glyceraldehyde prepared from L-arabinose.

D-Glyceraldehyde Dimedon

A solution of 0.30 gm. of D-glyceraldehyde in 60 ml. of phosphate buffer

*Aqueous acetic acid has been shown to be suitable for many lead tetraacetate oxidations (E. Baer, J. M. Grosheintz, and H. O. L. Fischer, *J. Am. Chem. Soc.* 61: 2607, 1939).

(containing 2 ml. of 1 *M* monopotassium phosphate and 1.2 ml. of 1 *N* sodium hydroxide) was treated with 1.1 gm. of dimedon dissolved in 10 ml. of ethanol, at 40°C. for five hours and then at room temperature for 18 hr. The crystalline product which settled out was filtered off, washed with water, and dried *in vacuo*. A second crop of crystals was obtained by concentrating the filtrate. The total weight of derivative was 0.82 gm. (73% yield); melting point, 194–200°C., undepressed by admixture with L-glyceraldehyde dimedon (10); $[\alpha]_D^{27} + 208^\circ$ (*c*, 0.6, ethanol). The infrared absorption spectrum of the derivative was identical with that of L-glyceraldehyde dimedon. Calc. for $C_{19}H_{24}O_8$: C, 68.24%, H, 7.84%; found: C, 68.26%, H, 7.81%.

L-Glyceraldehyde

L-Glyceraldehyde was prepared in 82% yield from L-sorbose by a procedure identical with that described above for preparing D-glyceraldehyde. Its specific rotation was $[\alpha]_D^{27} - 8.6^\circ$ (*c*, 3.6, water). An aliquot of the solution was concentrated, and the sirupy L-glyceraldehyde obtained was heated *in vacuo* at 55°C. for two hours and then redissolved in water; $[\alpha]_D^{27} - 14.3^\circ$ (*c*, 5.5).

The product appeared to be chromatographically pure and its infrared spectrum was identical with those of L- and DL-glyceraldehyde. It gave a 71% yield of L-glyceraldehyde dimedon; m.p., 197–198.5°C., undepressed by admixture with the derivative of the D-isomer; $[\alpha]_D^{27} - 210^\circ$ (*c*, 0.6, ethanol). Calc. for $C_{19}H_{24}O_8$: C, 68.24%, H, 7.84%; found: C, 68.27%, H, 7.78%.

DL-Glyceraldehyde

An equimolar mixture of D-fructose and L-sorbose (1.0 gm.) was oxidized under the conditions described above in the preparation of D-glyceraldehyde. The crude diester was taken up directly in 0.05 *N* sulphuric acid for hydrolysis of the ester groups, without previous extraction into ethyl acetate. The slightly turbid hydrolyzate was neutralized with the Dowex-1 resin and concentrated, yielding a clear, colorless sirup which was dried *in vacuo* over phosphorus pentoxide; weight 0.48 gm.; $[\alpha]_D^{27} 0^\circ \pm 0.1^\circ$ (*c*, 3, water). Sirupy DL-glyceraldehyde (42 mgm.), spread as a thin film on a microscope slide, solidified completely in two weeks at room temperature; weight, 38.5 mgm. (87% yield from starting material), melting point, 117–122°C. A mixed melting point with authentic DL-glyceraldehyde^{1*} (m.p. 145–147°C.) was 122–132°C. The infrared absorption spectrum and the X-ray diffraction pattern of the crystalline compound were identical with those of authentic crystalline DL-glyceraldehyde. Calc. for $C_3H_6O_3$: C, 40.0%, H, 6.71%; found: C, 39.58%, H, 6.65%. The compound contained 1% ash. A purer specimen was obtained by extracting DL-glyceraldehyde sirup with acetone, the acetone extract depositing crystals which melted at 138–140°C., undepressed by admixture with authentic DL-glyceraldehyde.

ACKNOWLEDGMENT

The authors thank Mr. J. Baignee for carbon and hydrogen analyses, Miss A. Epp for preparation of infrared spectra, and Mr. M. Mallard for X-ray diffraction analyses.

*Delta Chemical Works, New York 23, N. Y.

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RECEIVED SEPTEMBER 6, 1955.
 PRAIRIE REGIONAL LABORATORY,
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ON THE MEASUREMENT OF CHARGE ON INDIVIDUAL FIBERS

BY C. E. MOSSMAN* AND SIR ERIC RIDEAL

METHOD

The purpose of the experiments described here was to obtain a measure of the charge on a single fiber, by observing the deflection of such a fiber suspended in aqueous solution and under the action of an applied electric field. The effect of varying the field strength and the concentration of the different solutions was also investigated.

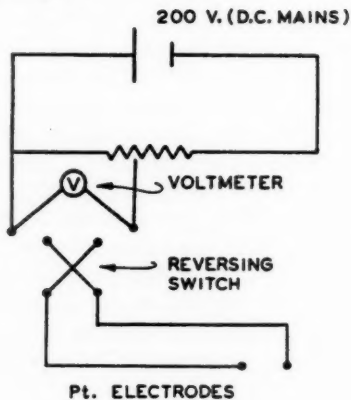


FIG. 1. Electric circuit.

The electric circuit used is shown in Fig. 1. The applied voltage could be varied from 0 to 200 v. (d-c.).

*Present address: Division of Building Research, National Research Council, Ottawa, Canada.

It was originally attempted to suspend the fiber (in this case, glass) by bending one end into the form of a hook or loop. The fiber was then suspended at right angles from a fine glass hook between the platinum electrodes. Difficulty was encountered because of friction at the point of contact of the hooks, which prevented the fiber from swinging freely. Deflections were measured by means of a travelling microscope.

A more satisfactory method of carrying out the measurements involved setting up a torsion balance. A fine quartz suspension was used as the torsion fiber. This was attached at the top to the torsion head with wax, and was held vertically by the weight of a quartz bead (W) glued to the bottom, as shown in Fig. 2. The fiber to be investigated (F), which was approximately 3 cm. in

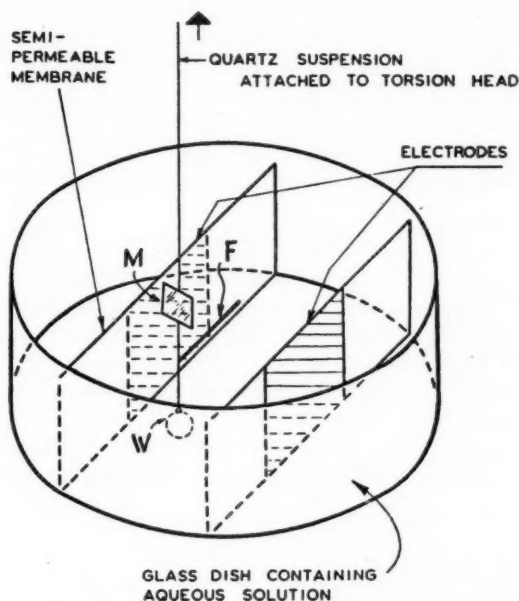


FIG. 2. Method of suspending the fiber between the electrodes.

length, was fastened at right angles to the quartz suspension. The whole system was arranged so that this fiber would be in the solution midway between the electrodes, which were of platinum foil. A small mirror (M) was attached to the quartz suspension just above the fiber, and a light beam was reflected from this mirror on to a circular scale. When the electrical field was applied, the degree of deflection could be measured by the twist of the calibrated quartz suspension, as indicated by the moving light beam.

It was immediately apparent that steady deflections could only be obtained in dilute solution, because of bubble formation and convection currents which interfered with the motion of the fiber when concentrated solutions were used.

The effect of convection currents was greatly reduced by separating each electrode from the fiber by a strip of semipermeable membrane, e.g., porous rubber. A flat electrophoresis cell was approximated by placing the fiber between two horizontally parallel glass slides (not shown in diagram). This also seemed to decrease the heating effect.

The quartz fiber was suspended inside a glass tube to eliminate any possible error due to draughts, and the whole system was placed on a wall mount to minimize vibration effects, to which it was extremely sensitive.

In order to use this torsion method, it is essential that the fiber whose deflection is to be measured be rigid. Glass and quartz were the fibers employed in the earlier exploratory runs; later terylene fiber was used.

The terylene fibers were cleaned by being placed in the thimble of a Soxhlet extractor, where they were washed with a propanol-water solution (60:40 by volume) for one hour. They were then stored in propanol until used. The fibers were always handled with tweezers in order to reduce risk of contamination.

The torsion constant (dynes/radian) for each quartz suspension used was determined by measuring the period of oscillation with and without a small body of known moment of inertia being attached to the quartz weight.

RESULTS

The results of these measurements were generally plotted as deflection (in centimeters of the circular scale, which was also calibrated in radians/cm.) against applied voltage. The actual potential gradient was not used (v./cm.). Since the electrode separation was always approximately 3.0 cm., it was felt that no great error was introduced by comparing results for different fibers at a given applied voltage.

An example of these plots for terylene in distilled water is given in Fig. 3, and shows that the deflections were reproducible in the opposite direction when

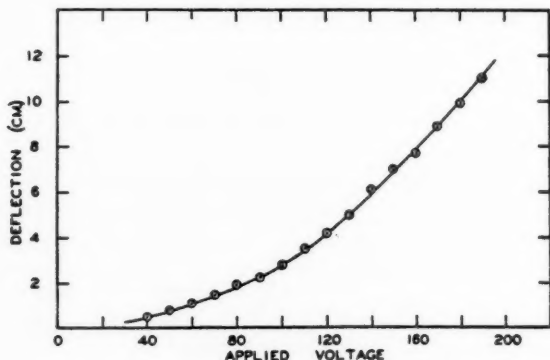


FIG. 3. Fiber deflection vs. applied voltage for terylene in distilled water. • Deflections to right; ○ deflections to left. Fiber length = 3.5 cm.; $\tau = 0.212$ dyne/radian; scale calibration = 1.94×10^{-3} radian/cm.

the direction of the current was reversed. Consecutive measurements on a given fiber were also reproducible. As might be expected, the deflection for a given applied voltage increased with increasing fiber length. The relation between deflection and applied voltage appeared to be nonlinear.

All the fibers were found to possess a negative charge in distilled water and dilute HCl solutions. This charge was reversed when dilute $\text{Th}(\text{NO}_3)_4$ was the electrolyte.

Some measurements were also carried out using solutions of such detergents as sodium octadecyl sulphate and sodium dodecyl sulphate. Although a small concentration of sodium octadecyl sulphate ($\sim 2 \times 10^{-4}$ molar) seemed to increase slightly the negative charge on the fiber over that observed in distilled water, further addition of the solution had no appreciable effect.

Results of a representative run using varying concentrations of sodium dodecyl sulphate are plotted in Fig. 4. In each case an initial increase in the negative charge was observed, followed by a continuous decrease with increasing detergent concentration.

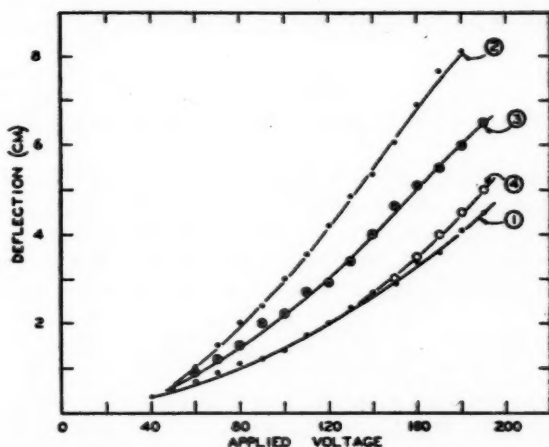


FIG. 4. Fiber deflection vs. applied voltage for terylene in (1) distilled water; (2) 4×10^{-4} M sodium dodecyl sulphate; (3) 8×10^{-4} M sodium dodecyl sulphate; (4) 2×10^{-4} M sodium dodecyl sulphate. Fiber length = 3.05 cm.; $r = 0.180$ dyne/radian; scale = 1.94×10^{-3} radian/cm.

Exploratory measurements were also made using solutions of orange II dye. Results of one run are shown in Fig. 5.

It had been hoped to investigate any variation in the charge on nylon fibers having different equivalent numbers of COOH and NH_2 groups. However the fiber samples obtained were not rigid, so that no convenient means of carrying out the measurements with the present system could be found.

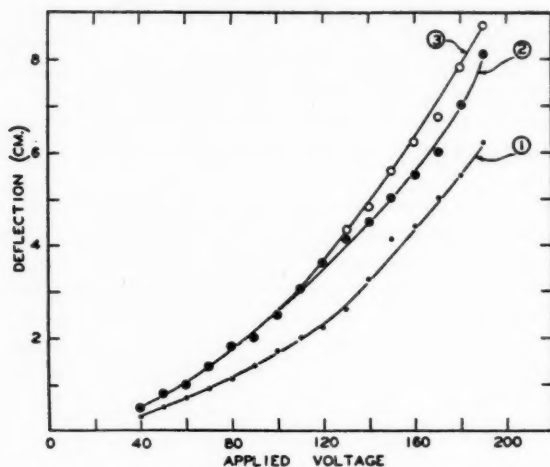


FIG. 5. Fiber deflection vs. applied voltage for terylene in: (1) distilled water; (2) 4×10^{-3} M dye; (3) 8×10^{-3} M dye. Fiber length = 3.2 cm.; $\tau = 0.19$ dyne/radian; scale = 1.94×10^{-2} radian/cm.

DISCUSSION

The effect is recognized as an electrokinetic effect, comparable to electrophoresis.

However, since the equilibrium point of the deflection rather than the rate of deflection has been determined, it must be expected that this would represent a measure of the charge on the fiber rather than of the zeta-potential. The charge, q (e.s.u./cm.²), would then be related to the fiber potential, ψ , which is not necessarily identical with the zeta-potential, by the equation:

$$q = \sqrt{\frac{2Dn\epsilon kT}{\tau}} \sinh\left(\frac{ze\psi}{2kT}\right).$$

Although the method appears to give a qualitative measure of the fiber charge, several difficulties are evident when an attempt is made to interpret the results quantitatively.

Considering first a spherical particle fastened to the end of an uncharged rod, the moving force on this particle would be:

$$F = E \cdot q,$$

where E is the applied potential gradient and q the charge on the particle. The restoring force may be expected to be equal to $\tau\theta/h$, where h is the distance from the sphere to the torsion wire, τ is the torsion constant, and θ is the deflection of the fiber from an initial position parallel to the electrodes.

However, in the case of a charged cylindrical fiber, it is difficult to know what the moving force will be. The force per unit of fiber surface may again be $E \cdot q$, but the correct expression for the total force would have to take into

account the fiber length. It would also be probable that the force on the part of the fiber nearest the torsion wire would be less than the force acting on the end of the fiber, which would be closer to the electrode.

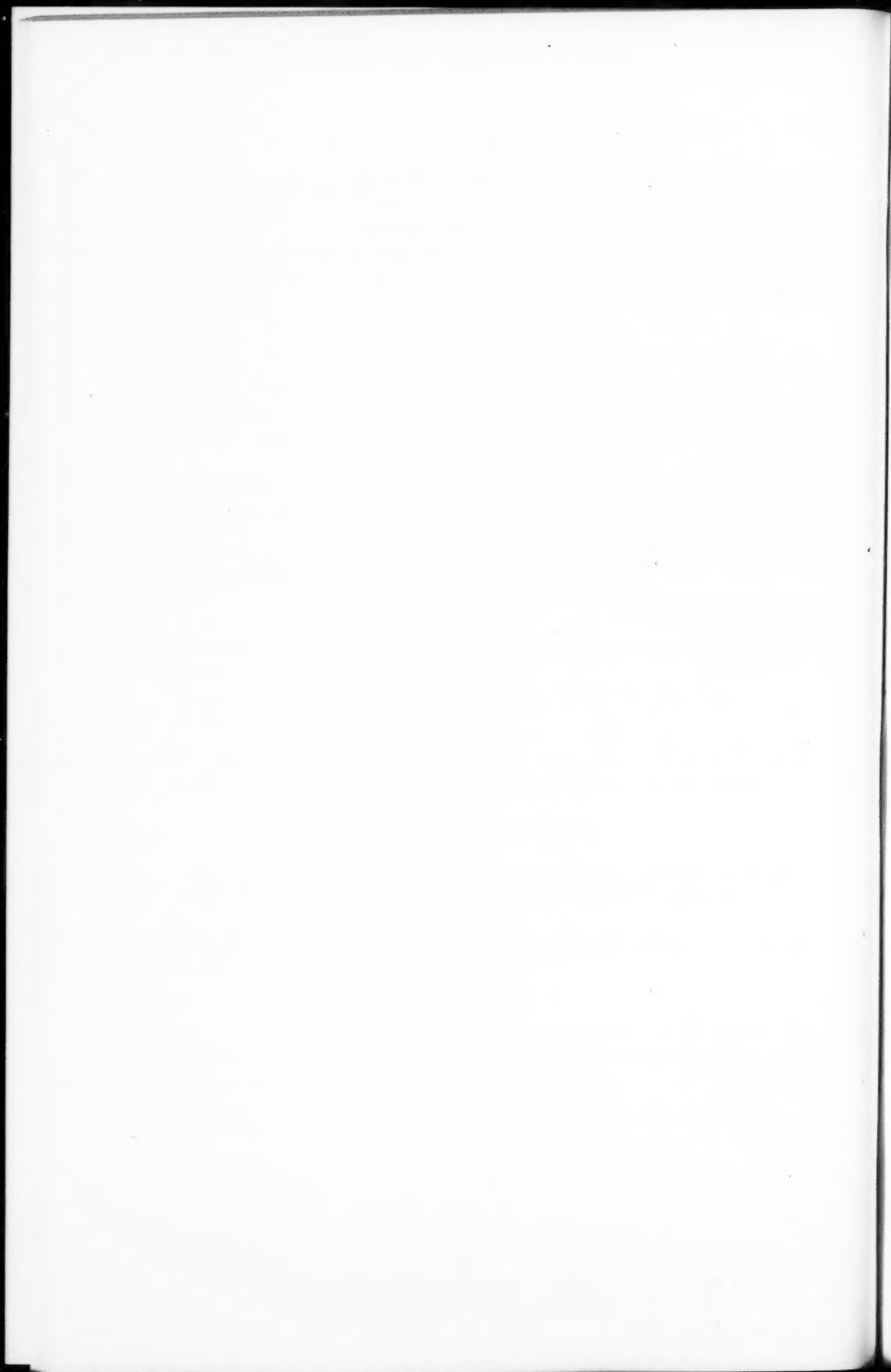
Taking the force per unit of surface as $E \cdot q \cdot \cos \theta$, it should be equal and opposite to the restoring force, $\tau \theta / h$, where h in this case is the length of the fiber. Then

$$E = \frac{\tau}{hq} \frac{\theta}{\cos \theta}$$

and $\theta / \cos \theta$, rather than θ , should be plotted against E . In actual practice, however, θ is so small that $\cos \theta$ is very close to unity over the whole range of potentials; the plots are therefore no more linear than those shown in Figs. 3 to 5.

Thus, while the method outlined here gives promise of being useful for the determination of relative charge densities, no absolute values can be calculated from the measurements already made until more is known of the nature of the forces acting on the fiber. In any further work along this line, it is recommended that a means of temperature control for the system be introduced.

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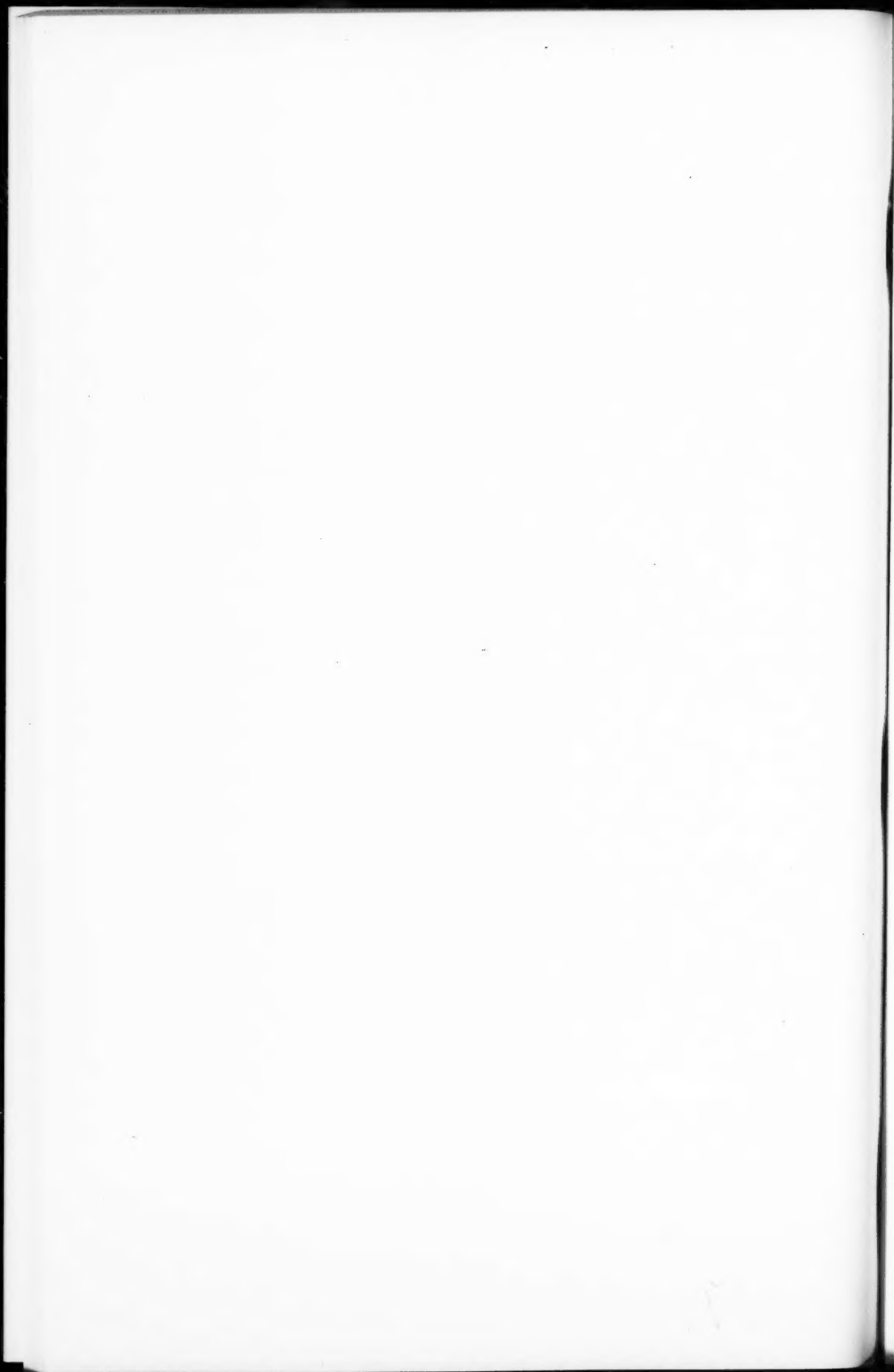
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